CARBON NANOTUBES: HIGH SOLIDS DISPERSIONS AND NEMATIC GELS THEREOF

GOVERNMENT RIGHTS

FIELD OF THE INVENTION

[0002]   The present invention is related to the field of carbon nanotubes. The present invention is also related to dispersions containing carbon nanotubes. In addition, the present invention is related to the field of materials and devices that contain carbon nanotubes.

BACKGROUND OF THE INVENTION

[0003]   .Carbon nanotubes are tiny fullerene-related structures of graphene cylinders having nanoscale diameters from about 0.7 to about 50 nanometers ("nm") and microscopic lengths from about 0.1 to about 20 microns ("μm"). Carbon nanotubes are readily synthesized catalytically from hot carbon vapor or by thermal decomposition of a carbon-containing gas or liquid. Different synthetic methods yield nanotubes with one or several

nested cylinders and different degrees of perfection. Various morphologies, tube shape, atomic conformations, and chemical compositions lead to a variety of uses. Chemical reactions inside or on the tube surface can be exploited for energy storage and drug delivery. The mechanical, electronic and thermal properties of carbon nanotubes enable a broad spectrum of applications including *inter alia* molecular electronics, nucleic acid and proteomic sequencing, high-strength composites, solar heat generation, energy storage and heat transfer.

[0004] The synthesis, characterization and useful applications of carbon nanotubes has been a fertile area of research for over twelve years, beginning with the discovery of multi-wall carbon nanotubes in 1991 by S. Iijima, as reported in *Helical Microtubules of Graphitic Carbon*, Nature **354**, 56 (1991). Shortly thereafter, several groups reported on the electrically conductive properties of carbon nanotubes in *Are Fullerene Tubules Metallic?*, J. W. Mintmire et al., Phys. Rev. Lett. 68, 631 (1992), in *New One-Dimensional Conductors - Graphitic Microtubules*, N. Hamada et al., Phys. Rev. Lett. 68, 1579 (1992), and in *Electronic Structure of Graphene Tubules Based on C_{60}*, R. Saito et al., Phys. Rev. B 46, 1804 (1992). In 1993, Overney et al. reported in the mechanical properties of carbon nanotubes in *Structural Rigidity and Low Frequency Vibrational Modes of Long Carbon Tubules*, Phys. D 27, 93 (1993). In the same year, S. Iijima et al. reported their synthesis of single-wall nanotubes in *Single-Shell Carbon Nanotubes of 1-nm Diameter*, Nature, 363, 603 (1993), and Bethune et al. reported on the synthesis of single wall carbon nanotubes in *Cobalt-Catalysed Growth of Carbon Nanotubes with Single-Atomic-Layer Walls*, Nature, 363, 605 (1993).

[0005] Reports of the use of carbon nanotubes in a variety of applications became more frequent as their preparation became more routine. For example, Rinzler et al. reported the use of nanotubes as field emitters in *Unraveling Nanotubes: Field Emission from an Atomic Wire*, Science 269, 1550 (1995). In 1996, ropes of single-wall nanotubes were reported in *Crystalline Ropes of Metallic Carbon Nanotubes* by A. Thess et al., Science 273, 483 (1996).

[0006] The quantum conductance of carbon nanotubes was reported in 1997 by Tans et al. in *Individual Single-Wall Carbon Nanotubes as Quantum Wires*, Nature, 386, 474 (1997). That same year, hydrogen storage in nanotubes was reported by Dillon et al. in *Storage of Hydrogen in Single-Walled Carbon Nanotubes*, Nature, 386, 377 (1997). The chemical vapor deposition (CVD) synthesis of aligned nanotube films was reported in

Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass, Z F Ren et al., Science, 282, 1105 (1998), and the synthesis of "nanotube peapods" was reported by Smith et al. in *Encapsulated C₆₀ in Carbon Nanotubes*, Nature 396, 323 (1998).

[0007] One of the more interesting properties of carbon nanotubes is their unusually high thermal conductivity, which can be useful for preparing materials for managing heat in a variety of useful systems and devices. For example, S. Berber et al. reported in 2000 *Unusually High Thermal Conductivity of Carbon Nanotubes*, Phys. Rev. Lett. 84, 4613 (2000). Another interesting property is their unusually high strength of macroscopically aligned nanotubes, as reported in *Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes,* B. Vigolo et al., Science 290, 1331 (2000).

[0008] In 2001, the integration of carbon nanotubes for logic circuits was reported in *Engineering Carbon Nanotubes and Nanotube Circuits Using Electrical Breakdown,* P.C. Collins et al., Science 292, 706 (2001). The intrinsic superconductivity of carbon nanotubes was also reported that year by M. Kociak et al., Phys. Rev. Lett. 86, 2416 (2001).

[0009] Recently in *Molecular Design of Strong Single-wall Carbon Nanotube/Polyelectrolyte Multilayer Composites,* Nature Materials, 1(3):190-194 (2002), Mamedov et al. described the preparation of a layered polymer/carbon nanotube composite made by attaching chemical groups to the nanotubes that form bonds with the polymer when the material is heated, or treated chemically.

[0010] As used herein, the term "carbon nanotube" refers to a variety of hollow, partially filled and filled forms of rod-shaped and toroidal-shaped hexagonal graphite layers. Examples of hollow carbon nanotubes include single-wall carbon nanotubes, multi-wall carbon nanotubes, carbon nanotoroids, branched carbon nanotubes, armchair carbon nanotubes, zigzag carbon nanotubes, as well as chiral carbon nanotubes. Filled carbon nanotubes include carbon nanotubes containing various other atomic, molecular, or atomic and molecular species within its interior. Examples include nanorods, which are nanotubes filled with other materials, like oxides, carbides, or nitrides. Examples of filled carbon nanotubes include carbon nanofibers having carbon within its interior. Carbon nanotubes that have hollow interiors have also be opened and filled with non-carbon materials using wet chemistry techniques to provided filled carbon nanotubes.

[0011] A single-walled carbon nanotube (SWNT) can be imagined as a rolled-up rectangular strip of hexagonal graphite monolayers. The short side of the rectangle becomes the tube diameter and therefore is "quantized" by the requirement that the rolled-up tube must

have a continuous lattice structure. The rectangle is typically oriented with respect to the flat hexagonal lattice to allow a finite number of roll-up choices. Two of these correspond to high symmetry SWNTs; in "zigzag" nanotubes, some of the C-C bonds lie parallel to the tube axis, while in "armchair" nanotubes, some bonds are perpendicular to the axis. Chiral nanotubes have a left- or right-handed screw axis, like DNA. Carbon nanotubes can also be nested together, one inside another to form so-called "nanocables". Carbon nanotubes can also have one end wider than the other to form so-called "nanocones". Carbon nanotubes in which the ends attach to each other to form a torus shape are commonly referred to as carbon "nanotoroids".

[0012]   The allowed electron wave functions of SWNTs are different than those of an infinite two-dimensional system of hexagonal graphite monolayers. In contrast the structure of a hexagonal graphite monolayer, the rolling operation imposes periodic boundary conditions for propagation around the circumference. This gives rise to a different electronic band structure for different symmetries of carbon nanotubes. As a consequence, SWNTs can be either metallic or insulating, with bandgaps in the latter typically ranging from a few milli-electron volts to about one electron volt.

[0013]   Carbon nanotubes can also be used bundled together or isolated. Nanotube bundles of many SWNTs with similar diameters are able to self-organize (order, i.e., "crystallize") during growth into a triangular lattice. Nanotubes may be isolated on surfaces, isolated in dilute fluid dispersions, and isolated in composite materials and devices. Bulk materials containing porous mats of nanotubes can be prepared from entangled bundles of carbon nanotubes.

[0014]   SWNT bundles are carbon-based materials into which heteroatoms or molecules can be inserted and removed. It is known that the proper choice of heteroatoms or molecules (alkali metals, halogen or acid molecules) can transform an insulating polymeric host into a doped semiconductor or even a metal, an example being sodium-doped polyacetylene. In a similar fashion, insulating molecular fullerene solids become superconducting upon addition of three alkali ions per molecule. Likewise, reversible insertion in graphite and SWNT bundles can be exploited for energy storage applications such as rechargeable batteries (e.g., Li-doped SWNT bundles) and "hydrogen containers" for use in hydrogen-burning vehicles.

[0015]   In view of the many fascinating novel electronic, thermal and mechanical properties of carbon nanotubes, many applications that will take advantage of these properties

will require large-scale manipulations of stable solutions of carbon nanotubes having high weight fractions of individual carbon nanotubes. For example, dispersions of individual carbon nanotubes will enable the use of a variety of solution-phase purification and separation methodologies. Accordingly, the preparation of high nanotube weight fraction solutions will facilitate a variety of processing steps performed on, and with, carbon nanotubes. Such processing steps include *inter alia* chemical derivatization, controlled deposition, microfluidic processes, fabrication of nanotube-based fibers, preparation of coatings and composite materials, as well as the fabrication of a variety of electronic, optical, micromechanical and microfluidic devices. Furthermore, high volume fraction nanotube solubilization will bring nanotube science into better contact with fundamental research on interactions and self-assembly in complex fluids. Unfortunately, as a result of the substantial van der Walls attractive forces between them, nanotubes readily aggregate and are difficult to keep individually dispersed in solution.

[0016]   Some progress has been made towards solubilization of carbon nanotubes in organic and aqueous media. Dissolution in organic solvents has been reported with bare SWNT fragments (e.g., 100 to 300 nm length) by Bahr et al., Chem. Commun., 2, 193, (2001) and by Ausman et al., J. Phys. Chem. B 104, 8911 (2000). Likewise, the dissolution of chemically-modified SWNTs has been reported by Chen et al., Science, 282, 95 (1998) and by Chen et al., J. Am. Chem. Soc. 123, 3838 (2001). Dissolution in water, important because of potential biomedical applications and biophysical schemes, has also been reported by Liu et al., Science 280, 1253 (1998), Bandow et al., J. Phys. Chem. B 101. 8839 (1997), Duesberg et al., Chem. Commun. 3, 453 (1998), Shelimov et al., Chem. Phys. Lett. 282, 429 (1998), and Bandyopadhyaya et al., Nano Letters 2, 25-28 (2002). Dissolution of carbon nanotubes by polymer wrapping has been reported by O'Connell et al., Chem. Phys. Lett. 342, 265 (2001) and by Star et al., Agnew, Chem. Int. ed. 41, 2508 (2002).

[0017]   Dissolution by chemical modification of the carbon nanotubes has been reported by Sano et al., Langmuir, 17, 5125 (2001), Nakashima et al., Chem. Lett. P. 638 (2002), and by Pompeo et al., Nanoletters 2, 369 (2002). Generally, the chemically modified carbon nanotubes are less desirable because their band structures can differ from the unmodified nanotubes. As well, chemically modified carbon nanotubes tend to be shorter than unmodified nanotubes. Indeed, carbon fibers having lengths greater than about 500 nm are desirable for introducing anisotropic properties in composite materials, as reported by Halpin et al. in Polymer Eng. Sci. 16, 344 (1976). Unfortunately, tube breakage typically

accompanies preparation of dispersions of carbon nanotubes longer than about 500 nm. Thus, there remains the problem of providing carbon nanotube dispersions that do not require chemical modification and which provide high volume fractions of long carbon nanotubes with minimal breakage.

[0018] Applications for carbon nanotubes generally fall into two categories: those requiring isolated carbon nanotubes and those requiring ensembles of carbon nanotubes. In applications using ensembles of carbon nanotubes, especially for composite materials, a high degree of nanotube alignment is desired. Aligning carbon nanotubes has been difficult, however. With few exceptions (Jin et al., Appl. Phys. Lett. 73, 1197 (1998) and Hadjiev et al., Appl. Phys. Lett. 78, 3193 (2001)), the vast majority of solution- and solid-phase mixtures are isotropic, as reported by Schadler et al., Appl. Phys. Lett. 73, 3842 (1998), Bower et al., Appl. Phys. Lett. 74, 3317 (1999), Sandler et al., Polymer 40, 5967 (1999), Andrews et al., Appl. Phys. Lett. 75, 1329 (1999), and Qian et al., Appl. Phys. Lett. 76, 2868 (2000). Accordingly, stable nematic-like phases of carbon nanotubes, especially of the SWNT variety, have been elusive. Thus, there also remains the problem of providing oriented ensembles of carbon nanotubes.

SUMMARY OF THE INVENTION

[0019] The present inventors have discovered that a particular class of surfactants is capable of providing stable dispersions of high concentrations of carbon nanotubes in aqueous media without requiring the aforesaid techniques of chemical modification or polymer wrapping. In a first aspect of the present invention, there are provided dispersions including an aqueous medium, carbon nanotubes, and at least one surfactant, the surfactant having an aromatic group, an alkyl group having from about 4 to about 30 carbon atoms, and a charged head group.

[0020] The present inventors have also discovered that a particular class of surfactants when used with an ultrasonication process is capable of providing stable dispersions of carbon nanotubes having reduced breakage of the carbon nanotubes. Thus, in a second aspect of the present invention, there are provided methods of preparing dispersions of carbon nanotubes, in which the methods include mixing an aqueous medium, carbon nanotubes, and surfactant in a low-power, high-frequency bath sonicator. In this aspect of the invention, the surfactant includes an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group.

[0021]   Within additional aspects of the invention there are provided compositions of carbon nanotubes that can be used in a variety of applications. In this aspect of the invention, there are provided compositions including carbon nanotubes and surfactant, wherein the surfactant has an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group.

[0022]   In another aspect of the invention, there are provided composite materials containing carbon nanotubes. In this aspect of the invention, the composite materials have a solid matrix and carbon nanotubes and surfactant dispersed within the solid matrix, the surfactant having an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a head group.

[0023]   In a related aspect of the invention, there are provided methods of preparing composite materials using the carbon nanotube dispersions provided herein. In this aspect of the present invention, there methods include dispersing carbon nanotubes and surfactant in a hardenable matrix precursor, and hardening the precursor. In these methods, the surfactant includes an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a head group.

[0024]   In another aspect of the invention, there are provided assemblies of carbon nanotubes. In this aspect of the invention, the assemblies include a substrate, and carbon nanotubes and surfactant adjacent to the substrate. In this aspect of the invention, the surfactant has an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group.

[0025]   In another aspect of the invention, there are provided methods of assembling carbon nanotubes on a substrate. In this aspect of the invention, the methods of assembling carbon nanotubes include contacting dispersions including an aqueous medium, carbon nanotubes and surfactant to a substrate. In this aspect of the invention, the surfactant includes an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group. These methods can be used, for example, in providing solid media for use in detecting chemical and biological substances. Thus, in a related aspect of the present invention, there are provided solid media having a substrate for receiving chemical compounds, biological materials, or both biological materials and chemical compounds for use in detecting chemical and biological substances. In this aspect of the invention the substrate includes carbon nanotubes and surfactant adsorbed thereon, the surfactant

comprising an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group.

[0026]   The present inventors have also discovered that the dispersed carbon nanotubes of the present invention can also be used to prepare nematic nanotube gels. In this aspect of the invention, the methods of preparing nematic nanotube gels include:

providing a dispersion of carbon nanotubes, solvent, gel precursor, and surfactant, the surfactant including an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group;

gelling at least a portion of the gel precursor to form a gel; and

subjecting the dispersion, the gel, or both the dispersion and the gel to an orienting field, the orienting field giving rise to a nematic orientation of said carbon nanotubes.

[0027]   The present inventors have also discovered compositions containing carbon nanotubes and gel precursors. In this aspect of the invention, the composition includes carbon nanotubes, gel precursor, and surfactant, the surfactant having an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028]   The invention may be understood by reference to the following description taken in conjunction with the accompanying drawings, in which:

[0029]   **FIG. 1** shows vials containing aqueous dispersions of SWNTs at 5 mg/ml after two weeks of incubation at room temperature with various surfactants. (A) SDS-HiPCO; (B) TX100-HiPCO; (C) NaDDBS-HiPCO. Carbon nanotube dispersions prepared with NaDDBS surfactant (C) are homogeneous whereas dispersions prepared with SDS (A) and TX100 (B) coagulate, forming a mass of aggregated nanotubes at the bottom of the vial.

[0030]   **FIG. 2** shows a tapping mode AFM image of TX100 stabilized laser-oven produced single-walled carbon nanotubes on a silicon surface. A dispersion of the carbon nanotubes was prepared at a concentration of 0.1 mg/ml by bath sonicator.

[0031]   **FIG. 3** shows the length and diameter distribution of HiPCO carbon nanotubes in various attempted dispersions. Data obtained from AFM images like the one in **FIG. 2**, after dispersion by bath sonicator and stabilized using three different surfactants. For original dispersion concentrations greater than 0.1 mg/ml, the dispersions were rapidly diluted to 0.1 mg/ml, and then spread over a silicon wafer for nanotube length distribution measurements using AFM. The contributions of nanotubes having lengths less than 50 nm are not reflected in these nanotube length distributions because of the limitation of the lateral

resolution of these measurements. **(a)** The number fraction of single nanotubes in a NaDDBS-HiPCO dispersion prepared at 0.1 mg/ml was about 74 ± 5 percent. **(b)** The number fraction of single nanotubes in a NaDDBS-HiPCO dispersion prepared at 20 mg/ml was about 63 ± 5 percent. **(c)** The number fraction of single nanotubes in a NaDDBS-HiPCO dispersion prepared at 10 mg/ml was about 61 ± 5 percent. **(d)** Repeat of **(c)** after sitting for one month (about 55 ± 5 percent, based on number, single nanotubes). **(e)** The number fraction of single nanotubes in a SDS-HiPCO dispersion prepared at 0.1 mg/ml was 16 ± 2 percent. **(f)** The number fraction of single nanotubes in a TritonX-100-HiPCO dispersion prepared at 0.1 mg/ml was 36 ± 3 percent.

[0032]   **FIG. 4** shows a schematic representation of how surfactant may adsorb onto the exterior surface of a tube. It is speculated that the alkyl chain groups of a surfactant molecule adsorb flat along the length of the tube rather than bend around the circumference. NaDDBS and TX100 disperse the nanotubes better than SDS because of their aromatic groups. NaDDBS also disperses carbon nanotubes better than TX100 because of its chargeable head group and slightly longer alkyl chain.

[0033]   **FIG. 5** shows the length and diameter distribution of 0.1 mg/ml laser-oven single-walled nanotube dispersions using NaDDBS as the surfactant and produced by tip and bath sonicators. **(a)** The low-power bath sonication method provided a high yield (90 ± 5 percent) of single (individual) carbon nanotubes; many individual carbon nanotubes had lengths longer than 400 nm post sonication, L_{mean} was about 516 ± 286 nm. **(b)** The tip-sonication technique gave significantly lower yield (50 ± 5 percent) and fragmented more nanotubes than in **(a)**; Only a few nanotubes having lengths larger than 400 nm were observed, and the mean length, L_{mean}, was about 267 ± 126 nm.

[0034]   **FIG. 6** shows a schematic of a NIPA gel structure (homogeneous) after NIPA monomer is polymerized in the presence of a gel initiator and cross-linker at 296 K.

[0035]   **FIG. 7** shows capillary nanotubes containing SWNT-NIPA gels before and after subjecting the gels to an orienting pressure field, which causes the gels to shrink. Capillary nanotubes containing initial nanotube concentrations of **(a)** 0.78 mg/ml and **(b)** 0.23 mg/ml appeared dark because the carbon nanotubes absorb light. A NIPA gel containing NaDDBS surfactant and no carbon nanotubes **(c)** was prepared to study the effects of the presence of the carbon nanotubes on the gel's shrinking. Here, the NIPA gel appears to shrink almost the same ratio whether or not the carbon nanotubes are present.

[0036]   FIG. 8 shows birefringence images of a carbon nanotube gel with initial nanotube concentration of 0.78 mg/ml, observed at different angles after sitting for four days. Images were taken with a fixed microscope bulb intensity and video gain and offset. Maximum birefringence was found when the samples was oriented 45 degrees with respect to the input polarizer pass axis. Liquid crystal like defects were observed near the edges of the nanotube gel, which are clearly visible when the gel was in vertical (0 degree) or horizontal (90 degrees) orientations. Greater nanotube alignment is observed near the gel edges. Evidently the director tends to align near the walls, perhaps as a result of boundary effects imposed by the walls. The central dark regions appear to be disordered in this figure; but when rotated on an axis coincident with the short edge of the sample by about 30 degrees, the central dark regions became bright, indicating that the central dark regions were at least partially ordered (not shown).

[0037]   FIG. 9 shows a summary of the effects of time and nanotube concentration on the alignment of nanotubes in NIPA gels. The bulb intensity and video gain offset were kept fixed. All of the samples were isotropic before shrinking. Birefringence was observed after the samples were shrunk upon subjecting them to an orienting pressure field.

[0038]   FIG. 10 shows capillary nanotubes with SWNTs-NIPA gel placed inside a vacuum jar, from which water slowly migrates out of the gel upon application of a pressure field using a vacuum pump.

[0039]   FIG. 11 shows images of carbon nanotubes inside NIPA gels that were isotropic before water extrusion at 0.46 mg/ml (a). As water was extruded from the gel, the carbon nanotubes began aligning along the flow direction of water and the gel became birefringent (b). At high enough initial concentration of nanotubes (0.46 mg/ml) in gel and after significant extrusion of water, some of the aligned nanotubes formed small ropes with the gel (c). The image (c) is a bright-field image at a higher magnification compared to (a) and (b).

[0040]   FIG. 12 shows carbon nanotubes that were aligned inside a NIPA gel using a nine Tesla magnetic field. Also observed are nanotube needles arising from the end-to-end chaining of multiple nanotubes.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0041]   Terms

[0042]   As used herein, the terms "nanotube" and "carbon nanotube" are used interchangeably.

[0043]   As used herein, the term "highly effective nanotube surfactant" refers to the class of surfactants, as exemplified by NaDDBS, which contains an aromatic group, an alkyl group having from about 4 to about 30 carbon atoms, and a charged head group. Unless indicated otherwise, use of the term "surfactant" herein refers to "highly effective nanotube surfactant".

[0044]   As used herein, the terms "single carbon nanotubes" and "individual carbon nanotubes" are synonyms that refer to freely dispersed carbon nanotubes in a dispersion that are not physically or chemically adsorbed, adhered, flocculated or aggregated to one or more other carbon nanotubes in the dispersion.

[0045]   The instant invention is based in part on an unexpected finding that particular surfactants having an aromatic group, an alkyl group, and a charged head group (the so-called "highly effective nanotube surfactants"), are capable of readily dispersing carbon nanotubes in aqueous media to provide colloidal carbon nanotubes. Also surprising is the discovery, as detailed herein, that a particular class of surfactants when used with an ultrasonication process is capable of providing stable dispersions of carbon nanotubes having reduced breakage of the carbon nanotubes. Another surprising discovery detailed herein is the ability to readily prepare composite materials and aligned nematic nanotube gels that contain dispersed carbon nanotubes. These novel features of the invention are advantageously used in various methods, devices, compositions and materials, as described further herein.

[0046]   Generally, a colloidal particle stabilized by charged surfactants will have a so-called "double layer" where counter ions (of opposite charge to the net charge on the particle) will be in excess surrounding each dispersed particle in the continuous (typically aqueous) phase. The degree to which the counter ions are in excess will decrease with increasing distance from the dispersed particle. The thickness of this double layer will be determined by the rate at which the net charge decreases with distance from the particle which is dependent on, *inter alia*, the ionic strength of the colloid. The colloid will be stable as long as the ionic repulsion between these double layers keeps the dispersed particles a sufficient distance apart for short range attractive forces (such as van der Waals forces) to be insignificant. If the double layer is too thin the dispersed particles can approach sufficiently closely for these attractive forces to predominate. Thus altering the ionic strength of the colloid will effect the thickness of the double layer and hence the stability of the colloid. When the ionic strength is raised to a particular amount the double layer is so thin there is

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effectively no ionic repulsion between particles and the forces between the particles are purely attractive which leads to the formation of a large solid mass. Hence adding a suitable ionic salt to a colloid (often called "salting out") will, at a certain concentration, suddenly produce an irreversible, catastrophic collapse of the dispersed particles into a distinct gelatinous clot or mass. Accordingly, the ionic strength of the aqueous media of the dispersions of the present invention are maintained at a level that maintains ionic repulsion between the carbon nanotube particles.

[0047]   Without wishing to be bound by a particular theory or mechanism of operation, the present inventors postulate that the superior dispersing capability of the highly effective nanotube surfactants can be explained in terms of graphite-surfactant interactions, alkyl chain length, head group size and charge that pertain particularly to those surfactant molecules that lie along the exterior carbon nanotube surface, parallel to the nanotube central axis. It is suspected that weaker surfactants like SDS (having a dispersing capability of less than about 0.1 mg/ml) have a weaker interaction with the carbon nanotube surface compared to highly effective nanotube surfactants because they lack an aromatic group. The aromatic group is believed to permit π-like stacking of the aromatic groups onto the graphene surface of the carbon nanotubes, which significantly increases the binding and surface coverage of the surfactant molecules. The alkyl group of the class of highly effective nanotube surfactant is suspected to lie flat along the exterior surface of the carbon nanotubes, especially for carbon nanotubes having small diameters on order of the size of the alkyl groups. Thus, it is energetically favorable for the alkyl groups (e.g., alkyl chains) to lie flat along the length of the carbon nanotubes rather than bend around its perimeter (e.g., circumference). The greater the surface contacts the alkyl group has with the carbon nanotube, the greater the favorable interaction the surfactant has for the nanotube. Finally, the charged head group of highly effective nanotube surfactants permits electrostatic repulsion that leads to charge stabilization of the nanotubes via screened Coulomb interactions which, in analogy with colloidal particle stabilization, may be significant for solubilization (i.e., dispersion) in aqueous media.

[0048]   The dispersions of the present invention include an aqueous medium and carbon nanotubes dispersed with at least one highly effective nanotube surfactant in the aqueous medium. Suitable surfactants have an aromatic group, an alkyl group, and a charged head group. While it is envisioned the aromatic group, the alkyl group, and the charged head group can be linked together in any chemically possible combination to provide a suitable

surfactant, typically the aromatic group is disposed between the alkyl group and the head group.

[0049] As the suitable alkyl groups contain carbon atoms, the skilled person will realize that a corresponding number of hydrogen atoms will also be bonded to the carbon atoms. The alkyl group can contain alkyl branches and rings, and will preferably include at least one linear alkyl chain. The number of carbon atoms in the alkyl group will typically be from about 4 to about 30, more typically from about 6 to about 20 carbon atoms, even more typically from about 8 to about 16 carbon atoms, and most typically from about 10 to about 14 carbon atoms.

[0050] Slight chemical variations to the alkyl group, especially where the number of carbon atoms is greater than about 12, are also envisioned as within the scope of the present invention. For example, the alkyl group may contain one or several chemical groups or unsaturated covalent bonds. Examples of such a chemical variation include additional atoms besides carbon and hydrogen that are bonded to the alkyl group (e.g., nitrogen, oxygen, or sulfur) and one or more unsaturation sites bonded to the alkyl groups (e.g., alkene and alkyne groups). The addition of such chemical variations can typically be such that the adsorption of the alkyl group to the carbon nanotube is not so grossly affected so that adsorption is otherwise prevented.

[0051] While any type of aromatic group is envisioned to be suitable for the highly efficient nanotube surfactants used in the present invention, suitable aromatic groups will typically be capable of π-like stacking onto the surface of the carbon nanotubes. π-like stacking refers to the overlap of π (pi) bonds of the aromatic group of the surfactant with the π bonds of the carbon nanotubes, which provides electron delocalization. Such hydrophobic interactions typically produces an energy minimum that favors non-covalent adsorbtion of the surfactant on the nanotube surface. The highly effective nanotube surfactants are typically capable of non-covalently adhering to said carbon nanotubes. Many aromatic rings known in the chemical arts are suitable for use in the surfactants. Typical aromatic groups will have a carbocyclic aromatic ring, a heterocyclic aromatic ring, or any combination thereof include two or more covalently linked together. Typically, carbocyclic aromatic rings include benzenes, naphthalene, biphenylene, biphenyl, and anthracene, as well as their C_1-C_{10} alkyl and alkene analogs known in the art, such as toluene, xylene, and vinyl benzene. A preferred carbocyclic ring is benzene. Suitable heterocyclic aromatic rings are typically carbocyclic rings having one or more carbon atoms substituted with an atom other than carbon. Typical

atom substitutes in heterocyclic aromatic rings include oxygen, sulfur, and nitrogen. The conditions of aromaticity can be met by many nitrogen-, oxygen-, and sulfur-containing ring groups. Heterocyclic aromatic ring groups have chemical properties similar to those of benzene and its derivatives. Examples of suitable heterocyclic aromatic ring groups include pyridine, purine, pyrimidine, pyrazine, pyridazine, pyrrole, imidazole, 1,3,4-triazole, tetrazole, furan, indole, oxazole, isoxazole, thiophene, thiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,3,5-trizene, quinoline, isoquinolene, acridine, and any combination thereof.

[0052]   While any type of charged head group is envisioned to be suitable for the highly efficient nanotube surfactants used in the present invention, suitable charged groups will typically be capable of carrying a positive or negative charge in aqueous media. Suitable charged head groups also capable of being electrostatically shielded from each other in aqueous media to affect dispersion. Accordingly, suitable charged head groups include any cationic, anionic, or amphoteric group that is known to be useful in preparing surfactants and dispersants for use in preparing aqueous particles dispersions. Examples of suitable anionic groups include sulfate groups and carboxylic, sulfonic, phosphoric and phosphonic acid groups which may be present as free acid or as water-soluble ammonium or alkali metal salts. Typically, the alkali metal salt will have a counterion selected from the Group IA elements, such as sodium, and potassium salts, e.g. sodium carboxylates and sulfonates, or any combination thereof.

[0053]   Combinations of anionic groups are also possible. Surfactants having an anionic charged head group may further contain one or more cationic groups as long as it has an overall anionic charge. If the surfactant is to have predominantly a cationic charged head group, then the reverse is true. Examples of suitable cationic head groups include sulfonium groups, phosphonium groups, acid addition salts of primary, secondary and tertiary amines or amino groups and quaternary ammonium groups, for example where the nitrogen has been quaternized with methyl chloride, dimethyl sulfate or benzyl chloride, typically acid addition salts of amines/amino groups and quaternary ammonium groups.

[0054]   The highly efficient nanotube surfactants are derived from synthetic and natural sources and preferably are water-soluble or water-dispersible. Many suitable surfactants are commercially available from various companies, such as The Akzo Nobel Company in The Netherlands (http://www.se.akzonobel.com/misc/ProductOverviewSurfactantsEurope.pdf). In a preferred embodiment, the surfactant includes anionic surfactants like alkylaryl sulfates and alkylaryl

ethersulfates, alkylaryl carboxylates, alkylaryl sulfonates, alkylaryl phosphates and alkylaryl etherphosphates. Typical anionic surfactants includes, sodium butylbenzene sulfonate, sodium hexylbenzene sulfonate, sodium octylbenzene sulfonate, sodium dodecylbenzene sulfonate, sodium hexadecylbenzene sulfonate, and preferably sodium dodecylbenzenesulfonate, and combinations thereof. Suitable surfactants preferably include an alkaline salt of a C_n alkyl benzene sulfonate, where n is between about 8 and about 16.

[0055] Examples of suitable surfactants having a cationic head group include cocobenzyldimethylammonium chloride, coco(fractionated)benzyldimethylammonium chloride, di(hydrogenated tallow)benzylmethylammonium chloride, and (hydrogenated tallow)benzyldimethylammonium chloride. Suitable cationic surfactants include those containing at least one quaternary ammonium compounds. Further suitable cationic surfactants include quaternary di- and polyammonium compounds.

[0056] In certain embodiments of the present invention, the surfactant contains a plurality of alkyl groups that are bonded to the aromatic group, an example being two alkyl chains attached. Typically, however, the surfactant will have a single alkyl chain.

[0057] In other embodiments of the present invention, the surfactant may further contain one or more hydrophilic chains. The one or more hydrophilic chains may be disposed on the surfactant in any combination, for example a hydrophilic chain may be connected to the charged head group, the aromatic group, or the alkyl group. A hydrophilic chain may also be disposed between any two of the charged head group, the aromatic group, or the alkyl group, e.g., a hydrophilic chain could separate the charged head group from the aromatic group. In these embodiments, the hydrophilic chains could function as a spacer. Suitable hydrophilic chains include polymers of alkyloxide monomers, such as ethyleneoxide and propyleneoxide, wherein the degree of polymerization is at least two.

[0058] Any type of carbon nanotube can be dispersed using the methods and surfactants as described herein. Although not an exhaustive listing of all known types of carbon nanotubes that can be used, a number of suitable carbon nanotubes that can be used in various embodiments of the present invention include the following: single-wall carbon nanotubes, multi-wall carbon nanotubes, armchair carbon nanotubes, zigzag carbon nanotubes, chiral carbon nanotubes, carbon nanofibers, carbon nanotoroids, branched nanotubes (e.g., as disclosed in U.S. Patent No. 6,322,713, the details pertaining to the preparation branched nanotubes is incorporated by reference herein), carbon nanotube "knees", coiled carbon nanotubes (L. P. Biro et al., Mat. Sci. and Eng. C 19 (2002) 3-7), or

any combination thereof. Many types of carbon nanotubes are commercially available. Several procedures known in the art are capable of synthesizing a variety of carbon nanotubes. For example, multi-wall carbon nanotubes can be made by the arc method known in the art and SNWTs can be made by the high-pressure carbon monoxide ("HiPCO") method known in the art and supplied commercially by Carbon Nanotechnologies, Inc. (Houston, Texas). SNWTs can be synthesized by the laser-oven method and supplied commercially by Tubes@Rice (Rice University, Houston, Texas). Carbon nanotoroids can be made by the HiPCO and laser-oven methods. Branched nanotubes can be made according to U.S. Patent No. 6,322,713, the details pertaining to the preparation of branched nanotubes is incorporated by reference herein. Carbon nanofibers are commercially available from Electrovac GesembH, Klosterneuberg, Austria. Carbon nanofibers typically are hundreds of micrometers long having diameters from about 70 to about 500 nm, having greater than about 100 square meters per gram (m^2/g) active chemical surface area. Chemical vapor deposition (CVD) methods are also capable of synthesizing carbon nanotubes.

[0059]   While the carbon nanotubes that are useful in the present invention have mostly carbon atoms, it is envisioned that at least a portion of the carbon atoms may be substituted with any of a variety of non-carbon atoms. Likewise, while chemical modification of the carbon nanotubes is not typically required for practicing the present invention as described herein, nevertheless, the carbon nanotubes may be chemically modified. In this regard, chemical modifications may include functionalization with any of a variety of chemical functional groups and molecules as known and practiced in the nanotube art.

[0060]   The highly effective nanotube surfactants enable the preparation of aqueous dispersions having very high concentrations of dispersed carbon nanotubes. Although any concentration of carbon nanotubes in the dispersion is possible, generally the nanotube concentration will be less than about 500 mg/ml, more typically less than about 200 mg/ml, even more typically less than about 100 mg/ml, even further typically less than about 50 mg/ml, and most typically less than about 25 mg/ml. Although very small concentrations of carbon nanotubes can be prepared according to the present invention, for example less than about 0.001 mg/ml, the nanotube concentration is typically at least about 0.001 mg/ml, more typically at least about 0.01 mg/ml, even more typically at least about 0.1 mg/ml, and even further typically at least about 0.5 mg/ml. Accordingly, the nanotube concentrations can be varied over a wide range for a variety of applications.

[0061]   In certain embodiments of the present invention, the carbon nanotube dispersions will have a high number percentage of individual carbon nanotubes. In these embodiments, the number percentage of single carbon nanotubes is typically at least about 50 number percent based on the total number of carbon nanotubes longer than 50 nm. This counting "cut-off" of 50 nm is conveniently selected based upon analytical procedures for measuring the length distribution of carbon nanotubes as described hereinbelow, e.g., using atomic force microscopy (AFM) coupled with computer software techniques for counting individual nanotubes. In other embodiments the number percentage of single single-wall carbon nanotubes is typically at least about 75 percent, and in other embodiments this percentage is at least about 90 percent. The present invention is not limited to the use of such a counting cutoff, as it will be readily apparent to those skilled in the art in view of the present disclosure that other counting methodologies and analytical instrumentation may be conveniently selected.

[0062]   In certain embodiments it is desirable that the mean length of a plurality of carbon nanotubes is typically at least about 120 nm. In embodiments where longer carbon nanotubes are desired, the mean length of the carbon is at least about 300 nm, and even at least as high as about 500 nm. When single carbon nanotubes are desired, the number percentage of single carbon nanotubes greater than 50 nm in length in the dispersions will typically be at least about 50 percent. As used herein, the term "mean length" typically refers to the mean end-to-end distance along the axis of cylindrical-shaped carbon nanotubes. For carbon nanotoroids, the term "mean length" refers to the mean of a the outside diameters of a plurality of toroids, i.e., the mean of the diameters of the outer circles. For branched carbon nanotubes, the term "mean length" refers to the mean of the longest distance from one branch end to another branch end. Other measures of length for various forms of nanotubes will be apparent from their respective forms.

[0063]   While any type of carbon nanotube can be dispersed according to the methods as provided herein, in a preferred embodiment of the present invention the carbon nanotubes are single-walled carbon nanotubes (abbreviated herein as "SWNT"). While the SWNTs are readily dispersed as aggregates of two or more SWNTs using the surfactants and methods described herein, it is typical that a portion of the SWNTs will be dispersed as single SWNTs. When single SWNTs are present in the various inventions as described herein, in certain embodiments it is desirable that the mean length of the collection of single SWNTs is typically at least about 120 nm. In embodiments where longer single SWNTs are desired, the

mean length of the single SWNTs can be at least about 300 nm, and even at least as high as about 500 nm. When single SWNTs are desired, the number percentage of single SWNTs greater than 50 nm in length in the dispersions will typically be at least about 50 percent.

[0064]   In certain embodiments of the present invention stable dispersions of carbon nanotubes typically include a surfactant to disperse and stabilize the nanotube particles. The amount of surfactant needed will vary depending on the surfactant's composition, the aqueous media, the chemical nature of the carbon nanotubes, and the total surface area of the carbon nanotubes that are to be dispersed. In various embodiments the present invention, the weight ratio of carbon nanotubes to surfactant is typically in the range of from about 5 : 1 to about 1 : 10. More surfactant is typically needed to increase the stability of the dispersions. The term "stability" used herein refers to the ability of the dispersed nanotubes to remain dispersed in solution without aggregation or flocculation. A high degree of stability is typically evidenced by a dispersion with little or no flocculation or aggregation developing upon standing for more than two weeks in a sealed vessel at ambient conditions. High degrees of stability are commonly achieved according to the methods of the present invention when the weight ratio of nanotubes to surfactant is in the range of about 1 : 5 to about 1 : 10. High degrees of stability are important for use in products in which liquid dispersions commonly stand for at least a week prior to their use (e.g., electronic chemicals processing of liquid photoresists). Lower degrees of stability can be achieved with lower relative amounts of surfactant. For example, a weight ratio of nanotubes to surfactant of about 3 : 1 can be used for keeping SWNTs dispersed for about a week in water. Thus, applications in which carbon nanotube dispersions are used in less than a weeks' time after preparation require even less surfactant. Because excessive amounts of surfactant can deleteriously alter various other properties in their applied use, it is typical to use just enough surfactant that permits dispersion and stability of the carbon nanotubes. Dispersions that are not stable (i.e., those in which the nanotubes begin to flocculate or aggregate upon standing at ambient conditions) are typically evidenced by at least one of the following: an increase in viscosity; an increase light scattering; formation of a liquid phase separation containing a nanotube-rich phase and a nanotube-poor phase; and formation of a solid clot or gel phase.

[0065]   In various embodiments of the present invention the carbon nanotubes can be stabilized using steric hindrance, charge stabilization, or both steric hindrance and charge stabilization to prevent the flocculation and aggregation of dispersed nanotubes. The carbon nanotubes are typically charge stabilized using one of the suitable surfactants described

herein. Without being bound by a particular theory, any of the suitable surfactants apparently disperse the carbon nanotubes through the operation of a portion of the alkyl group and aromatic group being adsorbed to the carbon nanotubes under the influence of dispersive forces, and by operation of the charged head group being situated in the aqueous solution to form a charge shield surrounding the carbon nanotube. Charge shielding of a plurality of nanotubes in the aqueous medium gives rise to a stable dispersion. Although many of the suitable surfactants described herein have a single alkyl group, certain embodiments the surfactants may have two or more alkyl groups. Likewise, the surfactant typically needs just one aromatic group, however two or more aromatic groups can be used. In a similar fashion, the surfactants can have more than one charged head group, although a single head group is typically required. Surfactants having any combination of two or more alkyl groups, two or more aromatic rings, or two or more charged head groups are also envisioned as useful for preparing the dispersions as described herein.

[0066]   The dispersions of the present invention include an aqueous liquid medium. As used herein, the term "aqueous medium" means including water. As used herein, the term aqueous liquid phase refers to the portion of the dispersion not including the surfactant and carbon nanotubes. While any amount of water in the aqueous medium can be used, the amount of water contained by the aqueous liquid phase is typically at least about 50 weight percent water, more typically at least about 70 weight percent water, even more typically at least 85 weight percent water, further typically at least about 90 weight percent water, and most typically at least about 95 weight percent, and in certain embodiments up to 100 weight percent water. While a majority of the aqueous medium will typically be water, it may also contain up to one or more solvents or solutes different than water. Typically, the aqueous liquid phase will include up to about 50 weight percent of a solvent different than water. This percentage is more typically up to about 30 weight percent, even more typically up to about 15 weight percent, further typically up to 1about 0 weight percent, and most typically up to about 5 weight percent of a solvent different than water. In certain embodiments no other solvents are present other than water in the aqueous liquid phase.

[0067]   Preparation of the dispersions of carbon nanotubes can be carried out using a variety of known particle dispersion methodologies, including but not limited to the use of high-shear mixers (e.g., homogenizers), media mills (e.g., ball mills and sand mills), and sonicators (e.g., ultrasonicators, megasonicators). In a more typical method of dispersing carbon nanotubes, there is provided a method that includes mixing an aqueous medium,

carbon nanotubes, and surfactant in a low-power, high-frequency bath sonicator. In carrying out this method, the mixing time is selected in the low-power, high frequency bath sonicator so that the carbon nanotubes become sufficiently separated from each other, contacted with the surfactant, and stabilized in the aqueous medium such that the carbon nanotubes remain substantially suspended in the aqueous phase upon cessation of input of the sonicator energy into the dispersion. Greater mixing times typically lead to greater degrees of dispersion of the carbon nanotubes. A suitable mixing time in a bath sonicator to achieve some level of dispersion of carbon nanotubes is typically in the range of about several minutes to about tens of hours, and is more typically at least about two hours, even more typically at least about four hours, even more typically at least about eight hours, and most typically in the range of from about 16 to about 24 hours. As used herein, the term "some level of dispersion" means that there has been a measurable diminution in aggregate size of carbon nanotubes, e.g., the preparation of single SNWTs from undispersed SNWT powder containing aggregates.

[0068]   In carrying out this method, suitable bath sonicators typically have a power in the range of from about five watts to about 75 watts. Likewise, suitable bath sonicators have an operating frequency in the range of from about 20 kilohertz ("kHz") to about 75 kHz.

[0069]   The methods of preparing the dispersions of the present invention can be carried out with any one or a combination of surfactants as described herein. The present methods can also be carried out wherein a minor portion of the surfactants used to be other surfactants known in the art, e.g., those not containing at least one of an alkyl group, and aromatic group, or a charged head group. In one embodiment of carrying out the present method, more than half of the surfactant based on weight will include an alkaline salt of a C_n alkyl benzene sulfonate, where n is between about 8 and about 16.

[0070]   In certain embodiments of the present invention, the mixing time is typically selected to give rise to at least about 50 number percent of the dispersed carbon nanotubes being single SWNTs. In these embodiments, it is also typical that the mixing time is selected to give rise to the mean length of single SWNTs being at least about 300 nm, and more typically at least about 500 nm. In carrying out these embodiments, the concentration of the surfactant based on the total volume of the dispersion is typically less than the critical micelle concentration (CMC) of the surfactant in the aqueous medium. Even more typically, the amount of free surfactant in the aqueous medium portion of the dispersion is less than the CMC of the surfactant based on the total volume of the aqueous medium. As used herein, the critical micelle concentration is the concentration at which micelles of surfactant form upon

addition of surfactant to the aqueous medium. The critical micelle concentration typically varies with the composition of the surfactant, the composition of the aqueous medium, and the temperature of the aqueous medium.

[0071] In certain embodiments of the present invention, applications of the carbon nanotube dispersions require that the electronic properties of the dispersed carbon nanotubes are essentially the same as the electronic properties of the carbon nanotubes prior to mixing. This can be carried out using carbon nanotubes that are not chemically modified, such as unmodified SWNTs. Thus, in one embodiment of the present invention there are provided methods of preparing SNWT dispersions from unmodified SNWTs using the methods of the present invention.

[0072] In additional embodiments of carrying out the methods of the present invention, the dispersed carbon nanotubes can be further processed using one or more processing steps for to carryout any of a number of post-dispersion processing steps. One post-dispersion processing step is classifying the nanotubes by size. A related post-dispersion processing step includes one or more separation steps to separate the carbon nanotubes according to length, shape, diameter, type, or any combination thereof. In carrying out these methods any one or more of known methods capable of classifying particles or soluble macromolecules can be used. For example, in one embodiment of the present method, there is provided a further step of electrophoretically separating the dispersed carbon nanotubes. Although the additional separation step typically occurs after the nanoparticles are prepared, it is possible that separation may also occur prior to dispersion, during dispersion, or both prior to and during dispersion.

[0073] The aqueous medium of the dispersions described herein can be partially or fully removed from the dispersion. In another embodiment there is provided a composition having carbon nanotubes and surfactant comprising an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a charged head group. Typically, such compositions will have at least a portion of the surfactant adsorbed to the exterior surface of the carbon nanotubes. This is especially useful for preparing nanotube compositions in the form of a powder, film, pellets, or any combination thereof. Powder, particle and pellet forms of the composition can be advantageously used as additives in various materials, including paints, coatings, adhesives, plastics, composites, and various engineering materials. Additional binder materials can be added to hold powdery compositions as pellets or films. The compositions of nanotubes and surfactant may also be mixed with a non-aqueous liquid,

such as an organic solvent, electrolyte, or oil to prepare oil-based carbon nanotube dispersions.

[0074] The composite materials of the present invention suitably include a solid matrix, carbon nanotubes and surfactant dispersed within the solid matrix. Suitable solid matrix materials include a polymeric material, a ceramic material, a metal oxide material, a metallic material, a semiconducting material, a superconducting material, an insulating silicon-containing material, and any combination thereof. Suitable polymeric materials include a linear polymer, a branched polymer, a crosslinked polymer, a grafted polymer, a block co-polymer, a ceramic precursor, or any combination thereof. Typically the solid matrix material includes a curable polymer resin precursor that can be hardened upon subjecting the resin to light, heat, radiation, or time for ambient curing. Suitable ceramic materials include any of a variety of ceramic materials that are suitably derived using sol-gel techniques. Examples of such ceramic materials include silicon dioxides, titanium dioxides and aluminum oxides. Typical sol-gel precursors that can be mixed with the carbon nanotube dispersions and compositions of the present invention include silicates for the preparation of silica gels, as well as a variety of silanes, silicones, germanes, alkoxides, tin compounds, lead compounds, metal organic compounds, for preparing any of a variety of known sol-gel solid matrix materials. Many sol-gel precursors are commercially available from a variety of suppliers, such as Gelest, Inc., Morrisville, Pennsylvania, and The E. I. DuPont Company, Wilmington, Delaware.

[0075] Composites of the present invention can have a variety of forms, and can take the form of a pellet, powder, or film. Such composite materials can be further processed into a variety of engineering materials and coatings.

[0076] Methods of preparing the composites typically include dispersing carbon nanotubes and surfactant in a hardenable matrix precursor, the surfactant including an alkyl group having from about 4 to about 30 carbon atoms, an aromatic group, and a head group; and hardening the precursor. In these methods, suitable hardening of the precursor typically includes curing the precursor with at least one of light, heat, radiation and time. Typical hardenable matrix precursors having these capabilities include any of the well-known cross-linkable organic-based multifunctional monomeric and oligomeric precursors, such as epoxies, polyesters, and ethylenically unsaturated styrenics. Sol-gel precursors are also useful as the hardenable matrix precursor for preparing ceramic metal oxide matrices.

[0077] In another embodiment of the composite materials of the present invention, the hardenable matrix precursor is a polymer capable of solidifying upon cooling to a temperature being lower than its glass transition temperature, its crystalline melt transition, its order-disorder transition temperature, or any combination thereof. A myriad of polymers having such properties are well-know in the art and can be used in the present invention. Examples of suitable polymers include but are not limited to polyolefins, polycarbonates, polyacrylics, polymethacrylics, polystyreneics, polyetherimides, polyamides, polyacrylamides, polyaklylacrylamides, polyimides, polyalkylimides, as well as random copolymers, block copolymers and blends thereof.

[0078] Assemblies having a substrate, and carbon nanotubes and surfactant adjacent to the substrate can also be fabricated according to the present invention. By use of the phrase "adjacent to the substrate" is meant that the carbon nanotubes and surfactant are limited in their physical location to an area in contact with, or in proximity to, the substrate surface. The assemblies are designed so that carbon nanotubes become arranged upon the surface of the substrate as they come in contact with the surface. Typically, the carbon nanotubes and the surfactant will be in the form of a dispersion in the presence of a solvent, such as an aqueous medium. Although this aspect of the present invention is typically carried out with an aqueous medium, it is not necessary for such a medium to be present. For example, the carbon nanotubes can assemble on the surface of a substrate using a suitable liquid-less mass transport system. A suitable liquid-less mass transport systems includes chemical vapor deposition processes.

[0079] In preparing the assemblies of the present invention the carbon nanotubes typically self-assembled on the substrate. The term "self-assembly" as used herein means that the carbon nanotubes arrange themselves in a fashion that is directed by their chemical, physical, and chemical-physical interactions between each other. Examples of self-assembly of carbon nanotubes includes alignment of the central axes of a plurality of carbon nanotubes in generally the same direction, herein referred to as "nematically-aligned". In assisting the orientation of the carbon nanotubes in a particular direction, the surfactant is typically adsorbed to the exterior surface of the carbon nanotubes, which permits molecular mobility and orientation of the carbon nanotubes in a particular direction under the influence of an orienting field. In the case of carbon nanotubes that self-assemble on surfaces from solution, and without being bound by a particular theory of operation, it is believed that the substrate surface imposes an boundary-directed confinement of normal molecular motion (i.e.,

Brownian motion), thereby giving rise to the assembly of carbon nanotubes in a particular orientation at the substrate surface.

[0080]   Assembling carbon nanotubes from one or more of the dispersions provided by the present invention on a surface of a substrate can be carried out by contacting a dispersion containing an aqueous medium, carbon nanotubes and surfactant to a substrate. The combination of carbon nanotubes and surfactant present in the dispersions of the present invention generally are capable of preferentially adsorbing on a variety of substrate surfaces. Preferential adsorbtion is generally driven by favorable surface energy thermodynamics that drive surfactant and carbon nanotubes from the dispersion out of solution and onto a surface. Carbon nanotubes can preferentially adsorb to the surface in an end-to-surface orientation that gives rise to self-assembly. Self-assembly will depend *inter alia* on a variety of parameters, including the self-organizing dispersive forces, the nature of the surfactant, the type and composition of the carbon nanotubes, the nature of the surface, and the quality of the dispersion. Self-assembled carbon nanotubes standing end-to-surface are capable of tightly packing close to the substrate surface, which typically reduces the overall enthalpy of the assembled system.

[0081]   Balancing the enthalpic components of the energetics of the system is its entropy. Entropy will typically drive the assembled system to disorganization. Because entropic components of the energy of a system decreases as the number of molecules in a system increases, a dispersion of longer carbon nanotubes will have a greater tendency to self-assemble on a substrate surface compared to a dispersion of shorter carbon nanotubes. In comparison to earlier methods, the methods of the present invention for preparing high weight fraction dispersions of relatively longer carbon nanotubes further enables the preparation of self-assembled carbon nanotube assemblies on substrate surfaces.

[0082]   One use of the carbon nanotubes of the present invention is to provide solid media that can be used in detecting chemical and biological substances. In this use, the solid media includes a substrate for receiving chemical compounds, biological material, or both biological material and chemical compounds for detection. Here, the substrate typically includes carbon nanotubes and surfactant adsorbed thereon, the surfactant comprising an alkyl group having between about 6 and about 30 carbon atoms, an aromatic group, and a charged head group. In one embodiment, the solid media are prepared by adsorbing surfactant to the exterior surface of the carbon nanotubes, the carbon nanotubes and surfactant adsorbed to the substrate. Typical substrates for solid media for detecting a variety

of substances include both organic and inorganic porous materials, such as polymeric materials, ceramic materials, zeolites and ion-exchange resins. In certain embodiments of the solid media of the present invention, it will be advantageous for the carbon nanotubes to be self-assembled on the substrate. In this embodiment when the carbon nanotubes are pointing their ends away from the surface, their ends are readily capable of attaching chemical and biological substances for analysis.

[0083] In a related embodiment, the solid media includes carbon nanotubes that are capable of adsorbing protons to give rise to a detectable signal. In this embodiment, the carbon nanotubes contain openings that are capable of receiving atomic, molecular, or both atomic and molecular species within their interior spaces.

[0084] In a related embodiment, the solid media includes carbon nanotubes that are chemically functionalized to adsorb specific biological material or chemical compounds to give rise to a detectable signal. A variety of chemical functionalization schemes are known in the separations literature, a number of which are capable of modifying the surfaces of carbon nanotubes. Specific examples include the addition of nucleic acids that hybridize with genetic material, acidic moieties that bind basic moieties of chemical compounds, basic moieties that bind acidic moieties of chemical compounds, proteomic and enzymatic fragments for binding proteins, and antigens for binding viruses.

[0085] Composites of aligned carbon nanotubes, especially containing single wall carbon nanotubes (SWNTs), are among the most sought after materials in nanotube science and technology. The present inventions are capable of providing such composite materials, especially those containing large domains of oriented SWNTs referred to herein as nematic nanotube gels. These composite materials are enabled by use of the highly efficient nanotube surfactants as described above.

[0086] The methods of preparing carbon nanotube gels according to the present invention typically include the steps of providing a dispersion of carbon nanotubes, solvent, gel precursor, and surfactant, gelling at least a portion of the gel precursor to form a gel, and subjecting the dispersion, the gel, or both the dispersion and the gel to an orienting field to give rise to a nematic orientation of the carbon nanotubes. By nematic orientation is meant that, on average, the carbon nanotubes are aligned in a particular direction. When aligned in a particular direction, the carbon nanotubes will typically have a finite order parameter greater than the fluctuation-induced order parameter at the order-disorder transition.

[0087]   In preparing the nematic nanotube gels, the concentration of the carbon nanotubes in the dispersion of carbon nanotubes, solvent, gel precursor, and surfactant, is sufficiently low so that carbon nanotubes remain substantially disordered in the dispersion. By substantially disordered is meant that a majority of the carbon nanotubes is capable of being oriented in any direction through action of Brownian motion. As the length of the carbon nanotubes increases, the concentration needed to achieve a substantially disordered dispersion typically decreases. Typically, this concentration is less than about 20 mg/ml, more typically less than about 10 mg/ml, and even more typically less than about 5 mg/ml, further typically less than about 2 mg/ml, and even further typically less than about 1 mg/ml, the concentration being based on the total weight of the carbon nanotubes, solvent, surfactant, and gel precursor. Likewise, the concentration of carbon nanotubes in the dispersions for preparing nematic nanotube gels will typically be at least about 0.001 mg/ml, more typically at least about 0.01 mg/ml, even more typically at least about 0.1 mg/ml, and further typically at least about 0.5 mg/ml, the concentration being based on the total weight of the carbon nanotubes, solvent, surfactant, and gel precursor.

[0088]   In several embodiments of the present invention the nematic nanotube gels may contain SWNTs having a particular degree of single dispersed nanotubes, a particular mean length, or both a particular degree of single dispersed nanotubes and a particular mean length. In these embodiments, the number percentage of single SWNTs is typically at least about 50 percent, more typically at least about 75 percent, and even more typically at least about 90 percent. In these embodiments, the mean length of single SWNTs is typically at least about 120 nm, more typically at least about 300 nm.

[0089]   In preparing the dispersions of carbon nanotubes, solvent, surfactant, are typically first mixed to provide a weight ratio of carbon nanotubes to surfactant in the range of from about 5 : 1 to about 1 : 10. Typically the gel precursor is soluble in the solvent used, the solvent typically being an aqueous medium as described above. The addition of gel precursor to a dispersion of carbon nanotubes is typically carried out in a fashion so that the carbon nanotubes remain charge stabilized in the dispersion. This can be carried out using any one of, or a combination of a variety methods know in the art of preparing composite materials containing particle dispersions. For example, in one embodiment, a gel precursor which is soluble in the solvent can be slowly added to a carbon nanotube dispersion while agitating or sonicating the dispersion. In another embodiment, the aqueous media can be

removed to form a powdery material, which is simultaneously or subsequently dispersed into a gel precursor.

[0090]   Suitable gel precursors used in the present invention can be any of a variety of monomer, oligomer, polymer, sol-gel ceramic precursor, or any combination thereof. Many types of materials are known to those skilled in the art of composites and are commercially available. Suitable polymer gel precursors will typically be soluble at their use concentration in the dispersion of carbon nanotubes, solvent, surfactant, and gel precursor prior to hardening. Typically, for the purposes of hardening the composite materials, the gel precursor will contain a monomer that is polymerizable via chain growth, step-growth, or any combination of chain-growth and step-growth polymerization mechanisms. Suitable monomers capable of chain-growth polymerization mechanisms contain at least one ethylenically-unsaturated chemical group. Examples of ethylenically unsaturated monomers include acrylic monomers, alkylacrylic monomers, acrylamide monomers, alkylacrylamide monomers, vinyl acetate monomers, vinyl halide monomers, diene monomers, styrenic monomers, or any combination thereof. Examples or ceramic gel-precursors suitable in this embodiment of the present invention are indicated above.

[0091]   In various embodiments using a polymer gel precursor, a crosslinker may also be included. Crosslinkers typically have two or more functional groups capable of covalently bonding to two or more polymer chains, such as any of the many multi-ethylenically unsaturated monomers that are well known in the polymerization art. The polymer gel precursor may further include an initiator, such as a free-radical initiator that is suitable for the initiation of chain polymerization of ethylenically unsaturated monomers. Various free-radical initiators are commercially available. Various suitable free-radical initiators are thermally-activated as well as activated by light such as UV radiation. The polymer gel may further include an accelerator. Accelerators are typically used to reduce the activation energy required by any of the initiation, polymerization and crosslinking (e.g., curing) processes. Many accelerators are well-known in the polymerization art, such as the teaching of the use of organophosphorus compounds for accelerating the curing of epoxy resin compositions, in U.S. Patent No. 6,512,031, the portion of which pertaining to the curing of epoxy resins is incorporated herein by reference thereto.

[0092]   Suitable orienting fields that can be used to nematically align the carbon nanotubes include pressure fields, magnetic fields, thermodynamic fields, electric fields, electromagnetic fields, shear fields, gravitational fields, as well as any combination thereof.

Suitable thermodynamic fields include any type of thermodynamic perturbation on the dispersion that gives rise to a volumetric phase transition. Examples of thermodynamic perturbations include a change in temperature, a change in composition, a change in pressure, and any combination thereof.

[0093] In one embodiment, a thermodynamic field is used to nematically align carbon nanotubes by changing the temperature of the gelled carbon nanotube dispersion to give rise to a volumetric phase transition. Here, the volumetric phase transition gives rise to a decrease in volume of the solvent-gel system, thus resulting in a volume-compression transition. In this embodiment, the carbon nanotubes are typically first dispersed at low volume fraction in a gel having zero or a very low degree of order. A volume-compression transition of the gel is typically applied to induce the randomly-dispersed carbon nanotubes to become aligned, which gives rise to a greater degree of order in the system. Hallmark liquid crystalline defects in these materials are typically observed, as well as a novel buckling of the walls accompanying defect formation arising from the disorder (i.e., isotropic) to order (i.e., nematic) transition. This transition from an isotropic to a nematic phase is typically concentration-dependent, which can be quantitatively measured by analysis of the tube order parameter.

[0094] Volumetric phase transitions used in the present invention typically arise from a change in temperature. While the change in temperature may arise from a lowering of the temperature, the volumetric phase transition typically arises from an increase in temperature. Generally, the volumetric phase transition arises from an incompatibility between the gel and the solvent. For example, this incompatibility between the gel and the solvent typically results from a decrease in a specific attractive interaction. An example of specific attractive interactions that can decrease upon the increase of temperature is hydrogen bonding. In one embodiment, when the gel is a polymer gel comprising a network, and the volumetric phase transition arises upon increasing temperature, the polymer network effectively becomes hydrophobic and solvent is expelled from the gel. The expelling of solvent from the gel reduces the overall mass of the system. In view of the fact that density typically remains invariant, a decrease in volume occurs that results in a volume-compression transition.

[0095] As will be appreciated by those skilled in the polymer gel art, the properties of polymer gels depends on a variety of parameters, including the nature and composition of the solvent. Because controlling hydrophilic-hydrophobic interactions with temperature

relies upon the existence of hydrogen bonding interactions, in one embodiment of the present invention the solvent typically includes at least about 50 weight percent water..

[0096] After subjecting the dispersion to an orienting field to provide a thermodynamic phase transition that gives rise to two or more phases, the phases may be separated. An example of such separation is carried out in embodiments wherein a solvent-rich phase is removed that is expelled from the gel during or after subjecting the gel to a volumetric phase transition.

[0097] In embodiments in which the gel undergoes a volumetric phase transition, the ratio of the volume of the gel before the volumetric phase transition to the volume of the gel after the volumetric phase transition is typically in the range of from about 1.1:1 to about 30:1, and more typically in the range of from about 4:1 to about 16:1.

[0098] One of the properties of the nematic nanotube gels is that they will typically exhibit birefringence subsequent to subjecting them to the orienting field. Birefringence pertains to the nematic nanotube gel having an anisotropic refractive index, e.g., the refractive index of the nematic nanotube gel in the direction along the nanotube axes is different than the refractive index across the nanotube axes.

[0099] In addition to subjecting the dispersions containing nanotubes, solvent, surfactant, and gel precursors to thermodynamic phase transitions that gives rise to nematically oriented carbon nanotubes, the dispersions can also be subjected to other thermodynamic phase transitions in various embodiments of the present invention. In one such embodiment, the method can further include the step of micro-phase separating at least one component of the dispersion into nanotube rich/gel poor and nanotube poor/gel rich phases. In this embodiment of the present invention, the gel can be a polymer gel, and the micro-phase separating step can be carried out under conditions giving rise to polymerization-induced phase separation.

[0100] In another embodiment of the present invention, the orienting field is a pressure field giving rise to transport of at least a portion of the solvent out of the gel. In this embodiment, the gelled material containing the carbon nanotubes is typically confined to a restricted geometry vessel. Suitable restricted geometry vessels include capillary tubes, microchannels, nanochannels, and substrate surfaces. Substrates surface embodiments typically have thin films of gelled material being situated thereon. In this embodiment, the gel is typically confined to a restricted geometry vessel during transport of at least a portion of the solvent out of the gel. Typically, the gel remains confined to the restricted geometry

vessel after transport of at least a portion of the solvent out of the gel. In additional embodiments the gel may be confined to a restricted geometry vessel both during and after transport of at least a portion of the solvent out of the gel.

[0101]   In carrying out the embodiments of the present method wherein the orienting field is a pressure field, a suitable pressure field is the application of a pressure to the gel that is lower than the partial pressure of the solvent in the vapor phase. In this embodiment, one typically applies vacuum to at least one open end of the restricted capillary vessel. In this case solvent molecules entering the vapor phase are carried away towards the vacuum source, which gives rise to a decrease in the solvent concentration in the gel. The decreasing concentration in solvent results in an increase in carbon nanotube concentration. As the carbon nanotubes become more crowded, they align thus forming a nematic nanotube gel.

[0102]   In another embodiment of the method of the present invention the orienting field is a magnetic field for magnetically inducing alignment of carbon nanotubes in gel material. In this embodiment, carbon nanotubes are typically aligned inside gel materials by applying a magnetic field to the dispersion while the gel precursor is gelling. Typically the dispersion is confined to restricted geometry vessel, but such a vessel is not essential. Any type of magnetic field source can be used as long as the magnetic field strength is typically at least about 0.01 Tesla (T), more typically at least about 0.1 T, and even more typically at least about 1 T. A suitable magnetic field source is a strong permanent magnet, and more typically a superconducting magnet is used. The strongest magnets are permanent, superconducting, and pulsed magnets. Permanent magnets retain their magnetism for a long time. The neodymium-iron-boron magnet is a strong permanent magnet that can produce a field of about 0.1 T. Carbon nanotubes containing iron (e.g., as an impurity) readily align in a magnetic field of about 9 T. When the carbon nanotubes are substantially free of iron, a magnet field of about 20 T is typically required for alignment. Superconducting magnets are a type of electromagnet that produces a magnetic field from the flow of electric current through a material having essentially zero electrical resistance. A superconducting magnet can reach field strengths as high as about 13.5 T, and typical superconducting magnets that are readily used in this embodiment of the present invention have magnetic field strengths typically in the range of from about 1 T to about 9 T. A pulsed magnet provides brief, but extreme magnetic fields as high as about 60 T. The limit to the upper magnetic field strength is typically limited by the type of magnet that is used, which is typically less than about 60 T.

[0103]   The strength and duration of a suitable magnetic field that is required for orienting the carbon nanotubes in the gel will typically depend on the gel viscosity and the average length and concentration of the carbon nanotubes. In many applications the viscosity of the gel while the dispersion is being subjected to the magnetic field is typically in the range of from about 1 centipoise to about 5000 centipoise. Likewise, the concentration of carbon nanotubes in the dispersions containing gel precursor, nanotubes, surfactant and solvent is typically in the range of from about 0.01 mg/ml to about 500 mg/ml based on the total dispersion, and is more typically at least about 0.1 mg/ml, even more typically at least about 0.5 mg/ml, and typically less than about 200 mg/ml, more typically less than about 100 mg/ml, and even more typically less than about 30 mg/ml.

[0104]   In certain embodiments of the method of the present invention wherein a magnetic orienting field is used, at least a portion of the carbon nanotubes align end-on-end giving rise to carbon nanotube needles. In this embodiment, the method may further include the step of removing solvent from the gel to provide carbon nanotube needle composite materials.

EXAMPLES

[0105]   **High Weight-Fraction Carbon Nanotube Dispersions.** A method to disperse high weight-fraction carbon nanotubes in water is provided in these examples. A novel surfactant for this purpose, sodium dodecylbenzene sulfonate (NaDDBS), having a benzene ring moiety, a charged head group, and an alkyl chain, dramatically enhanced the stability of carbon nanotubes in aqueous dispersion compared to commonly used surfactants, e.g. sodium dodecyl sulfate (SDS) and Triton X-100 (TX100); dispersion concentrations were improved by approximately a factor of one hundred compared to the commonly used surfactants. The method used herein eliminates the need for high power tip- or horn-sonication and repeated centrifugation and decanting. A single step process is used, which includes mixing SWNTs with surfactant in a low-power, high-frequency sonicator. This sonication procedure enhances disaggregation of bundles of aggregated SWNTs with dramatically less tube breakage. Diameter distributions of nanotube dispersions at high concentrations (20 mg/ml), measured by AFM, show that a large number percentage of these nanotubes were SWNTs (about 61 ± 3%). Initial electronic measurements show that this method does not alter the electronic properties of the nanotubes. Single nanotubes prepared by these means in high concentration can be used for creation of novel composite materials,

for self-assembly of nanotubes on surfaces and in dispersion, and for use as chemical and bio-sensors in water.

[0106]   SWNTs were obtained in purified form from Carbon Nanotechnologies Inc. (HiPCO SWNTs, batch 79) and Tubes@Rice (laser-oven SWNTs, batch P081600). According to manufacturer speculations, the HiPCO samples were about 99 wt% SWNTs (0.5 wt% Fe catalyst) and the purified laser-oven nanotubes were greater than about 90 wt% SWNTs. Typically the nanotubes were mixed with surfactant and sonicated in a low- power, high-frequency (12 W, 55 kHz) bath sonicator for about 16 to 24 hours to provide a dispersion. In order to evaluate competing stabilization characteristics, the dispersing power of a range of surfactants was explored: NaDDBS ($C_{12}H_{25}C_6H_4SO_3Na$), sodium octylbenzene sulfonate (NaOBS; $C_8H_{17}C_6H_4SO_3Na$), sodium butylbenzene sulfonate (NaBBS; $C_4H_9C_6H_4SO_3Na$), sodium benzoate ($C_6H_5CO_2Na$), sodium dodecyl sulfate (SDS; $CH_3(CH_2)_{11}OSO_3Na$), Triton X-100 (TX100; $C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$; n about 10), dodecyltrimethylammonium bromide (DTAB; $CH_3(CH_2)_{11}N(CH_3)_3Br$), Dextrin, and poly(styrene)-poly(ethylene oxide) (PS-PEO) diblock copolymer. Of the surfactants tested, the dispersions prepared with NaDDBS and NaOBS were by far the most stable; dispersed nanotube concentrations in NaDDBS ranged from 0.1 mg/ml to 20 mg/ml, the highest tested. The resulting dispersions prepared with NaDDBS remained dispersed for at least three months; neither sedimentation nor aggregation of nanotube bundles was observed in these samples. In contrast, highly stable nanotube dispersions could not be prepared with the other additives at concentrations greater than about 0.5 mg/ml. With the exception of NaOBS, a close relative of NaDDBS, reliable disaggregated dispersions in the other surfactants required nanotube concentrations of less than about 0.1 mg/ml. Figure 1 contains images of the nanotube dispersions in NaDDBS, SDS, and TX100 at 5 mg/ml. The NaDDBS-nanotube dispersion is homogeneous whereas SDS-nanotube and TX100-nanotube dispersions have coagulated bundles of nanotubes at the bottom of their respective vials.

[0107]   Quantitative information about the distribution of the diameter and length of the dispersed nanotubes was measured using atomic force microscopy (AFM). An example of an AFM image used for this analysis, in this case of laser-oven nanotubes at a concentration of 0.1 mg/ml and stabilized by TX100, is shown in Figure 2. Surfactant stabilized nanotubes were deposited onto a silicon wafer. The tube surface density was sufficient for analysis when the dispersion nanotube weight fractions were 1 mg/ml; dispersions with greater weight fractions, e.g. above about 20 mg/ml, were rapidly diluted to

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1 mg/ml or 0.1 mg/ml and then spread over the silicon wafer for the AFM measurements. The AFM image quality was substantially improved by baking the resultant wafers at 180 °C for approximately 4 hours (or longer); apparently baking removes much of the surfactant from the wafer and from the nanotubes. AFM images were taken in tapping mode using a Nanoscope III Multimode (Digital Instruments Inc., Santa Barbara, CA). Digital Instrument supplied software was then used to derive the length and the diameter of the every accessible nanotube in the image. Nanotubes that were not entirely within an image were excluded. Tube diameters were derived from our height measurements, which had a resolution of about 0.1 nm; typically four separate height measurements were made for each tube and were then averaged. Tube lengths were determined within our lateral resolution of about 20 to 50 nm; it was difficult to accurately characterize nanotubes whose lengths were less than 50 nm, so their contributions are not reflected in the measured distributions. A summary of the AFM observations is given in Figure 3. About 300 nanotubes were examined for each distribution plot. The shaded regions define single nanotubes; 1.3 and 1.5 nm was used as the upper bound for a single tube diameter of the HiPCO and the laser-oven prepared nanotubes, respectively.

[0108] The first four distributions are for NaDDBS-HiPCO dispersions. Figure 3(a) shows that a NaDDBS-HiPCO dispersion prepared at 0.1 mg/ml was about 74 ± 5% single nanotubes. This yield changed modestly as a function of increasing nanotube weight-fraction, see Figure 3(b) and Figure 3(c). Furthermore, the distribution from the 10 mg/ml dispersion was measured after allowing it to sit for one month; the single-tube fraction did not change appreciably (about 54 ± 5%; Figure 3(d)). By contrast, HiPCO stabilized in SDS and TX100 at a concentration of 0.1 mg/ml had SWNT yields of about 16 ± 2% (Figure 3(e)) and about 36 ± 3% (Figure 3(f)), respectively. The mean length (L_{mean}) of single nanotubes for the four NaDDBS-HiPCO distributions was about 165 nm with a standard deviation between 75 and 95 nm. The number of longer nanotubes (i.e., greater than about 300 nm) was observed to decrease slightly in the samples that were diluted to about 1 mg/ml (distributions not shown). SWNT length distributions for SDS-HiPCO (L_{mean} about 105 nm ± 78 nm), and for TX100-HiPCO (L_{mean} about 112 nm ± 54 nm) were shifted a bit lower; generally many long SWNTs were not found using SDS or TX100.

[0109] The solubilizing capabilities (i.e., "dispersing power" or "dispersing capability") of the various surfactants was also investigated. Without being bound by any particular theory of operation, any successful dispersing method must reckon with the

substantial van der Waals attractions of bare nanotubes. A schematic of how the surfactants might adsorb onto the nanotubes is depicted in Figure 4; the nanotubes are stabilized by hemi-micelles that sheath the surface. The superior dispersing capability of NaDDBS compared to SDS (dispersing capability ≤ 0.1 mg/ml) or TX100 (dispersing capability ≤ 0.5 mg/ml) may be explained in terms of graphite-surfactant interactions, alkyl chain length, head group size and charge as pertains particularly to those molecules that lie along the surface, parallel to the tube central axis. It is suspected that SDS has a weaker interaction with the nanotube surface compared to NaDDBS and TX100, because it does not have a benzene ring. Indeed π-like stacking of the benzene rings onto the surface of graphite is believed to significantly increase the binding and surface coverage of surfactant molecules to graphite. Dextrin (dispersing power less than 0.05 mg/ml) and DTAB (dispersing power less than 0.1 mg/ml) also did not disperse nanotubes well because, it is believed, they do not have ring moieties. It is suspected that the alkyl chain part of surfactant molecules lies flat on the graphitic tube surface. Most of the surfactants of the present invention in these examples had alkyl chains with lengths of order 2 nm. Thus, when adsorbing onto a small diameter nanotube surface it is probably energetically favorable for the chains to lie along the length of the nanotubes rather than to bend around the circumference. This chain interaction distinguishes TX100 (8 carbon alkyl chain) from NaDDBS and SDS (both have 12 carbon alkyl chain). Longer chain lengths improve surfactant energetics, given similar ring and head groups. For example, sodium benzoate (no alkyl chain, dispersing power ≤ 0.01 mg/ml), and NaBBS (4 carbon alkyl chain, ≤ 0.1 mg/ml) have same ring and head group size as NaDDBS, but did not perform very well because of substantially shorter alkyl chain length. On the other hand, NaOBS (8 carbon alkyl chain, dispersing power up to 8 mg/ml) performed quite well. Sodium hexadecylbenzene sulfonate had a longer alkyl chain (16 carbons), but did not dissolve in water at high concentration (more than about 5 wt%) at room temperature -- surfactants having alkyl groups greater than about 16 carbons can be dissolved using elevated temperatures, by the use of solvents that are soluble in aqueous media, or both.

[0110] Without being bound by a particular theory of operation, the different responses of NaDDBS and TX100 probably arise from head group and chain lengths. The head group of TX100 (PEO chains) is polar and larger than NaDDBS (SO_3^-); its large size may lower its packing density compared to NaDDBS. Furthermore, the electrostatic repulsion of SO_3^- leads to charge stabilization of nanotubes via screened Coulomb interactions which, in analogy with colloidal particle stabilization, may be significant for

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dispersion (solubilization) in water compared to the more steric repulsion of the TX100 head group. Generally, added salt (NaCl) of greater than about 25 mM induced aggregation in the NaDDBS samples. PS-PEO diblocks, which had long PEO chains as head group, did not stabilize nanotubes well ($\leq$ 1.0 mg/ml).

[0111] The relative efficacy of different sonication techniques on the dispersion of nanotubes was investigated in the following examples. Tube length is a parameter that is desirable controlled in preparing SWNT dispersions; SWNTs with large lengths (e.g., greater than about 500 nm) are often desirable for introducing greater anisotropies into the properties of composites. The standard approach is to disperse nanotubes using a high power tip sonicator (1/8 inch, 6 W, 22.5 KHz) for short time (about 1 hour). For comparison, 0.1 mg/ml of HiPCO nanotubes and laser-oven nanotubes were prepared in NaDDBS, SDS and TX100, and the resulting length and diameter distributions were measured. Observations of these studies are summarized in Figure 5 for 0.1 mg/ml laser-oven nanotubes dispersed with NaDDBS. The nanotube dispersion prepared by bath sonication had very high yield (number percentage) of single nanotubes (about 90% ± 5%), a significant percentage of which were long single nanotubes with lengths longer than about 400nm (L_{mean} about 516 nm ± 286 nm), see Figure 5(a). Similar samples prepared by tip sonication (Figure 5(b)) had lower single SWNT yield (about 50% ± 4%), and L_{mean} about 267 nm ± 126 nm. These effects were not as pronounced in the HiPCO nanotube dispersions, apparently for the reason that the HiPCO nanotubes were already rather short compared to the laser-oven nanotubes.

[0112] **Uses of High Weight Fraction SWNT Dispersions.** The 100X increase in nanotube solubility, and the relatively smaller amount of tube fragmentation, makes a plethora of processing schemes for SWNTs more accessible, as listed here:

[0113] **Preparation of composites:** There is great interest in manufacturing composite materials with large tensile and torsional strength or better thermal or electrical properties. Long and relatively non-fragmented nanotubes can be readily incorporated into any polymer matrix to increase both the tensile and torsional strength, change thermal or conducting properties using the methods described herein. For example, nanotube dispersions were mixed with epoxies to improve the thermal property of epoxies. Here, a commercially-available epoxy emulsion (EPON-3510-W-60, Shell Chemical, emulsion of bisphenol-A epoxy dispersed in water, 60 wt. percent active solids) was mixed with a 20 mg/ml aqueous SWNT dispersion made according to the methods described above. 1 ml of the epoxy emulsion and 200 microliters of the nanotube dispersion was sonicated at 80 °C

using the above-described methods. Evaporating off the water provided 600 microliters of a liquid dispersion containing epoxy and the nanotubes dispersed therein. Curing agent (EPICURE-3234, Shell Chemical; EPICURE-9553, Shell Chemical) was mixed into the epoxy-nanotube dispersion, and curing was carried out by the "SONICURE" ™ (University of Pennsylvania, Philadelphia, PA) process. This process incorporated the simultaneous sonication and curing of the dispersion. This process provides localized heating and curing of the mixture (i.e. gel precursor), which hardens in about two to three minutes. The SONICURE ™ process advantageously helps to maintain the nanotubes dispersed in the epoxy resin during curing. The resulting nanotube composite was annealed for two hours at 120 °C to provide a composite having a solid matrix and the carbon nanotubes dispersed therein. In related examples the epoxy-nanotube-curing agent mixture was simply heated to 120 °C for curing.

[0114] **Electrical Conductivity of SWNT-Epoxy Composites:** The electrical conductivity of a SWNT-epoxy composite material made according to the above procedure was about 10^{-5} S/cm. The composite contained a concentration of about 0.05 mg of nanotubes dispersed per ml of composite material. Notably, this electrical conductivity is about 100 times larger than the value of the nanotube epoxy composite reported by Park et al., Chem,. Phys. Lett. Vol. 364, page 303, 2002, which had between 2 mg nanotubes per ml of composite material.

[0115] **Self-assembly to form a SWNT Monocrystal:** Now that stable dispersions of nanotubes can be prepared at high concentration, nanotubes can be assembled into 3-D crystals using graphite surfaces as templates and depletion interactions or convection as the driving force. Using convection as a driving force and graphite as a template, a single layer of highly organized pyrolytic graphite ("HOPG") strip was affixed to a glass cover slip. A SWNT dispersion made according to an earlier example was placed in a 5 mm diameter x 4 cm vial. The HOPG strip/cover slip was dipped into the dispersion in the vial at an angle. This assembly was placed in an oven at 50 °C to allow the water to evaporate. Capillary force apparently organized the nanotubes at the liquid-vapor interface as the water evaporated. Evaporation was completed after 4-5 days. This process initially provided a monolayer of nanotubes at the beginning of the evaporation process. Towards the end of the evaporation process, a large monocrystal of self-assembled nanotubes having a thickness greater than about one millimeter was formed. This monocrystal can be used in memory devices and display units.

[0116]   **Length, chirality sorting and purification:** Nanotubes of the present invention that are well covered by anionic surfactants in dispersion can be post-processed using electrophoresis to separate the nanotubes by length. The adsorbed surfactant molecules can function as "handles" that drag the nanotubes along the field through the electrophoresis gel. This method can also separate the nanotubes from impurities. Thus, this adsorption mechanism of the alkyl group of a surfactant can be used to sort armchair nanotubes (which are typically metallic) from zigzag or chiral nanotubes. Length sorting was carried out in a gel having large pore sizes. A column containing 0.5 percent agarose gel was prepared to provide a large pore size. A vertical column 30-40 cm long was prepared. An aqueous SWNT dispersion made according to an earlier example was poured in the top of the column and the nanotubes were recovered based on length. The size exclusion effect of the agarose gel permitted the longer tubes to exit the column first, thereby effecting separation by length. Narrow nanotube length distributions based on peak length were obtained, e.g., mean lengths of 500 nm +/- 20 nm were obtained.

[0117]   In a related example, the agarose gel is placed between electrodes, and a voltage of about two volts is applied across the electrodes to assist the separation of the nanotubes in the vertically-oriented column. In a horizontally-oriented column, separation is effected by placing electrodes at the column ends and applying a voltage of about 5-10 volts.

[0118]   **Controlled deposition on surfaces:** Carbon nanotubes are controllably placed on surfaces (e.g., positively charged silicon wafer) at any specific location using the aqueous nanotube dispersions as prepared in one of the earlier examples. The negatively charged surfactants enable circuit design with carbon nanotubes. A silicon wafer is patterned using any one of the known methods (e.g., via photoresist microlithographic methods) suitable for preparing a positively charged pattern on a substrate. The aqueous dispersion is coated onto the substrate and the nanotube-surfactant moieties adhere to the positively charged pattern. After deposition, the surfactants on the tube can readily be vaporized by baking the resultant wafer at 180 °C to leave patterned nanotubes on the substrate surface.

[0119]   Controlled deposition of the nanotubes is carried out as follows: A silicon wafer is coated with a suitable photoresist coating (e.g., acrylic-based polymer solution with a UV-activated initiator), and then patterned using e-beam or light. Depending on whether the photoresist is positive or negative, a micropattern is formed by subsequent treatment with solvent to remove the uncrosslinked photoresist. Aminopropyltriethoxysilane (APTS) is then vapor deposited onto the patterned wafer (one to two ml solution of APTS solution in

vacuum jar with wafer facing up; evacuate for 30 seconds to deposit APTS on the pattern). After APTS deposition, most of the APTS is removed by sonicating the wafer in DMF to provide a monolayer of APTS on the surface. Presence of the APTS monolayer (0.7 to 0.9 nm thick) is confirmed with ellipsometry or an AFM technique. The wafer is removed and dried and placed in HCl vapor to protonate the amine to form a positive charged surface. The wafer is submerged into nanotube dispersion for 6-12 hours, removed, and rinsed with water. The wafer is dried in a clean environment (ca. 6 hours), and submerged in solvent (e.g., acetone) to remove the photoresist. This procedure provides nanotubes patterned on a substrate, which is used to build circuits and sensors, as described herein.

[0120] **Chemical and bio-sensors:** The surfactants used in the present invention that have a charged head group containing SO_3 can be used for fashioning nanotubes into sensor devices for chemical and biological compounds. Nanotubes respond electronically to adsorption of charged atoms, such as a single hydrogen atom (i.e., a proton). The controlled deposition of carbon nanotubes as described above is carried out with a surfactant having a SO_3 charged head group. The nanotubes are used as is or with slight chemical modification to detect the level of analyte (e.g., NH_3 or NH_2) in a test sample. If the test sample is a portion of the atmosphere then the sensor is suitable for monitoring air pollution or minute contamination. In sensor applications, the surfactant is physically adsorbed to the nanotube surface. The SO_3 group binds chemically to the NH_3 in the sample. A microfluidic device is built containing a circuit that incorporates the SWNTs patterned in a region over which the sample liquid containing the analyte flows. The NH_3 component in a sample is absorbed onto the nanotubes. The nanotubes are connected to electrical contacts in the circuit, and a voltage (V) is applied and the current (I) is measured. When an analyte molecule is adsorbed onto the nanotubes, a change in the current-voltage (I-V) curve is used to detect the presence of a targeted analyte.

[0121] A variety of analytes can be detected using this sensor, including hydrogen (i.e., protons), ammonia, amine groups, CO and CO_2. Nanotubes with amine surface groups arising from the surfactants or chemically modified nanotubes can easily bind to different kinds of biological molecules and be constructed into bio-sensors. Nanotubes dispersed using surfactants having an amine group at the end, e.g., an ammonium group, are useful for binding and detecting biological molecules. In this example, a nanotube dispersion is prepared using a surfactant wherein the charged head group is capable of binding biological molecules (e.g., nucleic acids, proteins, and polysaccharides). For example, the amine form

of NaDDBS (i.e., the aromatic group is attached to a chargeable ammonia head group) is used in aqueous solution. Controlled deposition of the nanotubes is carried out in a microchannel device as described earlier. The bound nanotubes in the microchannel device are connected to electrical contacts in an array to monitor a plurality of I-V response curves for a plurality of nanotubes The measured I-V curve of the nanotubes changes depending on the binding of biological molecules, which is used to detect the presence of the same or different biological molecules. Different molecules are detected at different points in the array using different specific ligands attached to the nanotubes. For example, standard hybridization targeting assay techniques using a variety of nucleic acid ligands can be used to specifically detect targeted genetic material of a biological agent.

[0122] **Creating composites containing nanotubes via sol-gel reaction:** Nanotubes were dispersed using a bath sonicator as follows. 10mg of a 20mg/ml nanotube dispersion dispersed with 10mg/ml NaDDBS was added in a crucible to 90 mg of silica gel precursor in water, 40 wt. percent solids weight fraction (DuPont, Wilmington, Delaware). The pH was lowered to a value of about 4 by adding HCl. The system formed a ceramic composite gel material after five minutes without any visible macroscopic phase separation of nanotubes.

[0123] The ceramic composite gel material is subsequently annealed at elevated temperatures and pressures to provide a ceramic material. Annealing silica gel at 1100 deg C gives rise to ceramics having nanotube voids as the carbon nanotubes will burn off at this elevated temperature.

[0124] In another example, an alumina oxide gel precursor is substituted for the silica gel precursor as described above to provide a composite containing nanotubes dispersed in alumina gel. Alumina oxide gel precursors, 40 weight percent solids in water, are commercially available from DuPont, Wilmington, Delaware. The pH is lowered and the gel forms. The nanotube-alumina gel composite is annealed at temperature in the range of from about 300 to 450 deg C. At these lower temperatures the carbon nanotubes remain substantially intact to provide ceramic alumina composites containing dispersed carbon nanotubes.

[0125] **Creating thermoplastics with surfactant stabilized nanotubes in water:** Nanotubes were dispersed in water (20 mg/ml dispersed in water using 2 : 1 nanotubes to NaDDBS surfactant). These dispersions are emulsified in a non-aqueous solvent or oil phase to form aqueous emulsions of carbon nanotubes in non-aqueous phase (e.g., solvent or oil).

A non-aqueous phase containing 1.5 wt percent Span 80 (Sorbitan monooleate surfactant, Aldrich Chemical Co. Milwaukee, WI) in hexadecane solvent was prepared. The nanotube dispersion was micropumped in one channel of a microfluidic T cell having dimensions of 50 to 100 micron square capillaries as the non-aqueous phase was micropumped into a second channel of the T cell. An emulsion of aqueous nanotube dispersions in a non-aqueous phase was formed at the junction. Flow rates were in the range of from about 100 to 500 microliters per hour for both channels to form microdroplets of aqueous carbon nanotubes in the hexadecane solvent. The microdroplets were between 40 micron and 100 microns, depending on the channel size. The microdroplets were collected in a vessel, allowed to settle, and the excess solvent top layer was removed. Methyl methacrylate (MMA) monomer was dissolved in dimethylformamide (DMF) solvent (2 – 7.5 wt. percent MMA based on solvent). Ethyleneglycol diacrylate (EGDA) crosslinker, 0.5 to 1.0 wt. percent based on monomer weight, was added to the non-aqueous phase of the collected microdroplets. Polymerization was initiated in the non-aqueous phase using sodium persulfate (0.2 wt. percent based on monomer). Temperature was raised to 60 °C and polymerization continued for about several hours until gelation occurred. The polymer formed a gel matrix with the nanotubes embedded therein. The resulting material was subjected to elevated temperatures and reduced pressures to remove excess solvent and water. A black rectangular solid composite material having dispersed nanotubes in a plastic resin was obtained. This material can be heated above its Tg and the nanotubes oriented as described below.

[0126] **Overview of Alignment of SWNTs to Provide Nematic nanotube gels.** The following examples describe three methods used to align SWNTs inside a gel matrix to prepare nematic nanotube gels. To induce alignment of SWNTs in gels, SWNTs were dispersed at low concentration (≤ 0.78 mg/ml) in an aqueous N-isopropyl acrylamide (NIPA) gel precursor. Polymerization was initiated by chemical means at 295K. The pre-gel solutions were then loaded into rectangular capillary tubes and allowed to polymerize at 295 K. The polymerization process completed in about 1 hour. In the first example of creating nematic nanotube gels, the gel volume was reduced substantially by increasing its temperature; this volume phase transition arises when the polymer network in the gel becomes hydrophobic and water is expelled (and removed). If the initial nanotube concentration was sufficiently large, then the tubes aligned locally. In the second example, water was slowly evaporated out of the SWNTs-NIPA gel through the open ends of the capillary tubes. The flow of water out of the capillary tubes caused the nanotubes to align along the flow direction of water (the

long axis of the capillary tubes). In the third example, the capillary tubes with SWNTs-NIPA gel were placed inside a magnet immediately after the initiation of polymerization for the duration of the polymerization process. The nanotubes were aligned by the magnetic field and were locked in place by the gel. By varying the magnetic field strength, gel viscosity and polymerization time, it was possible to align the nanotubes, make nanotube needles with multiple nanotubes, and make long aligned ropes of nanotubes.

[0127] Dispersions of laser-oven SWNTs (obtained from Tubes@Rice) having greater than 90 wt% SWNTs were prepared as described in the previous examples with NaDDBS. These nanotube dispersions had very high yield of single tubes (about $90 \pm 5\%$) with average length L_{mean} about $516 \, nm \pm 286 \, nm$. It is not critical to use laser-oven SWNTs in these examples; HiPCO nanotubes (Carbon Nanotechnologies Inc., batch 79; L_{mean} about $165 \, nm \pm 95 \, nm$) have also been used and similar results were obtained.

[0128] Most, but not all of these experiments used a gel of polymerized N-isopropyl acrylamide monomer (NIPA; 700 mM), N,N'-methylenebisacrylamide (cross-linker agent; 8.6 mM), ammonium persulfate (initiator; 3.5 mM) and N,N,N', N'-tetramethylethylenediamine (accelerator at 295 K; 0.001% v/v). All components were obtained from PolySciences Inc. (Warrington, Pa) and were used without further purification. To prepare SWNTs-NIPA gels, SWNT dispersions and all gel reagents were first mixed, except the initiator, in water. The SWNT concentrations ranged from 0.04 mg/ml to 0.78 mg/ml (the NIPA monomer did not gel well when the SWNT concentrations were higher). The gel initiator was then added to the mixture which was then vortexed for 15 seconds. The polymerization took about an hour. The vortexed pre-gel solutions were loaded into rectangular capillary tubes with inner dimensions (length x width x thickness) of about 4 cm x about 4 mm x about 0.2 mm and a wall thickness of about 0.2 mm. Fig. 6 shows a schematic of gel structure after polymerization in the presence of cross-linker.

[0129] To align the nanotubes outside of a magnet, the pre-gel solution were polymerized at 295 K for about three hours. To align the tubes inside of a magnet, the capillary tubes with SWNTs-NIPA gel were placed inside a 9 Tesla magnet and at 295 K for longer than the required time for complete polymerization (about 2 hrs). The initial gelation process appeared to lock nanotubes into place, producing a dilute tube distribution with random location. The tube orientation was random when the gel polymerized outside of a magnet; the tube orientation was parallel to the applied field when gel polymerized inside a

magnet. Apparently, the tubes could not diffuse over long distances in the gel, but could reorient and move short distances with relatively small energy cost.

[0130]   Images depicting birefringence in the nematic nanotube gels were obtained with samples situated between crossed-polarizers in a microscope on a rotating stage. The crossed-polarizer measurement is sensitive to birefringence in the sample, which arises when nanotubes align. The aligned regions appear bright in the image; isotropic regions appear dark. For clarity the pass axes for the input and output polarizers were set to be along the x and y directions respectively; the light transmission direction was along z; the sample was rotated in the xy-plane. By rotating the stage, information about the direction of alignment of nanotubes was obtained. By keeping the microscope bulb intensity and the video gain/offset the same for the full set of images, semi-quantitative information about the degree of alignment of nanotubes in the NIPA gel was obtained from the relative intensity differences between various images or regions within an image. An increase in the degree of nanotube alignment was manifested as an emerging bright domain or an increase in the brightness of a domain. Bright-field images of the nanotube needle or ropes in the nematic nanotube gels were obtained without cross-polarizers. The birefringence and the structures within the sample were visualized using a Leica DMIRB inverted optical microscope with a 10X, 5X and 1.6X air objectives. The samples were imaged using a CCD camera (Hitachi, model KP-M1U, 640x480 pixels) and recorded directly into a computer hard-drive using a 8-bit video frame grabber (model CG7, Scion Corporations, Frederick, Maryland).

[0131]   The magnet used to align the nanotubes was a super-conducting magnet (Quantum Design, San Diego, CA) for which the magnetic field could be varied between -10 Tesla to +10 Tesla and the temperature could be varied between 4 K and 373 K. To align the nanotubes, the capillary was loaded inside the magnet immediately after the polymerization of NIPA gel was initiated. This remained inside the magnet at 9 Tesla for longer than the duration of polymerization (about two hours).

[0132]   **Method 1: Local alignment of SWNTs by shrinking the SWNTs-NIPA gel.** To induce nematic-like structures in SWNTs-NIPA gel, the capillary tubes with SWNTs-NIPA gel were immersed inside glass vials containing 20mM Trizma buffer (Sigma-Aldrich, St.Louis, MO) and placed the entire sample assembly inside an oven at 323 K. The polymer network in the gel became hydrophobic around 323 K. The gel then reduced its volume by expelling water and therefore, the effective volume fraction of the locked SWNTs in the gel increased. For sufficiently large initial nanotube concentrations the tubes aligned

locally. The capillary tube containing shrunk SWNT-NIPA gel was taken out of the buffer, the expelled water was removed, and the sample imaged under the microscope. Removal of expelled water prevents the gel from swelling to its pre-shrunk volume as the gel temperature is lowered to room temperature (about 295 K) and the polymer networks became hydrophilic. This local aligning of SWNTs in NIPA gel is referred to herein as a "quasi-isotropic-nematic" transition.

[0133] Fig. 7 is a photograph of the SWNTs-NIPA gels and NIPA gels with surfactant alone (7.8 mg/ml NaDDBS) before and after shrinking. Typical pre-shrunk sample dimensions (length x width x thickness) were about 4 cm x about 4 mm x about 0.2 mm and shrunk dimensions were about 2 cm x about 2 mm x about 0.1 mm. The sample in Fig. 7(a) had a high initial nanotube concentration (0:78 mg/ml) and the material underwent a quasi-isotropic-nematic transition immediately after shrinking. The sample in Fig. 7(b), by contrast, initially contained a dilute mixture of nanotubes (0.23 mg/ml) and the quasi-isotropic-nematic transition was not observed immediately after shrinkage. It is evident from the photograph that the volume change ratio before/after shrinking is large (about eight times); the shrunken gels in Fig 7(a) and 7(b) also appear darker, apparently for the reason that the tube concentration is higher and the tubes absorb visible light.

[0134] In Fig. 8 one of the concentrated samples is depicted as a function of angle. All the images were taken with fixed microscope bulb intensity and video gain and offset. This sample had an initial tube concentration of 0:78 mg/ml, and was allowed to sit for 4 days after shrinking. The gel exhibited a maximum birefringence when its edge was oriented 45 degrees with respect to the input polarizer pass axis. Liquid crystal like defects were observed near the edges with the sample; visible when the sample was in vertical (0 degree) or horizontal (90 degrees) orientations. Apparently there was greater tube alignment near the gel edges; the director tends to align near the walls, perhaps as a result of boundary effects. The darker regions in the center of the sample could indicate tube disorder or tube alignment in the z-direction. To distinguish these possibilities the sample was rotated between 10 to 60 degrees about the y-axis. Significant changes in the central birefringence profile were not observed, however. Most likely, the central dark regions were disordered.

[0135] Features of our concentration- and time-dependent observations are summarized in Fig. 9. The bulb intensity and video gain/offset was the same as before. All of the samples were isotropic before shrinking; light transmission was zero. Birefringence was observed in samples that shrank. Twenty minutes after shrinking, the highest initial

concentration (0.78 mg/ml) sample exhibited birefringence. As time passed though, the samples slowly evolved. Alignment clearly started at the edges of the sample and migrated inward. After one day the sample critical concentration for birefringence near the edge was approximately 0.54 mg/ml. After 2 days the critical concentration for birefringence had decreased further. The degree of nematic alignment in the samples was found to increase and the critical concentration for nematic alignment decrease, respectively, with increasing time after shrinking the gel.

[0136]   These quasi "isotropic-nematic" transitions apparently differ from lyotropic transitions of suspended hard rods in some respects. The transition nanotube volume fractions were lower than expected based on nanotube behavior in water alone, suggesting the gel network plays a significant role in increasing the effective tube interaction, local concentration, or both.

[0137]   In the above examples, the gel polymerization temperature was kept at 295 K. At this temperature, the gel network and the tube distribution within the gel was homogeneous. However, when polymerizing the NIPA monomer at a higher temperature (about 304 K), the nanotubes can micro-phase separate into regions of nanotube rich/gel poor regions and nanotube poor/gel rich regions. At high enough nanotube concentrations, the nanotubes in nanotube rich/gel poor region can align to become nematic. Such behavior is observed in other rod-like molecules (e.g., fd virus) in NIPA gel.

[0138]   **Method 2: Nanotube alignment via water extrusion from SWNTs-NIPA gels.** To extrude water from SWNTs-NIPA gels, the capillary tubes containing the gels were placed inside a vacuum jar, which was slowly evacuated using a vacuum pump. The experimental setup is shown in Fig. 10. Initially, the nanotubes inside the gel were isotropic and the sample under cross-polarizers appeared dark as shown in Fig. 11(a). The slow vacuuming of the chamber caused water from the center of the samples to extrude (migrate) to the open ends of the capillary tubes and being evaporated off. The SWNTs-NIPA gel then started to shrink at the middle of the capillary tubes in width and thickness, as shown in Fig. 11(b). The flow out of water caused the nanotubes to align along the flow direction of water (the long axis of the capillary tubes) and the shrunk region became birefringent, as shown in Fig. 11(b). Eventually most of the water was extruded from the gel and the entire gel became birefringent. Typical sample dimensions before and after water extrusion were (length x width x thickness) about 4 cm x about 4 mm x about 0:2 mm, and about 2:8 cm x about 2 mm x about 0:1 mm, respectively. By varying the rate of water extrusion from the SWNTs-

NIPA gels, or the initial nanotube concentrations in gel, or both, SWNTs were able to align or make small ropes as shown in Fig 11(c).

[0139]   **Method 3: Magnetic field induced alignment of nanotubes in NIPA gels.** To align nanotubes inside NIPA gels, capillary tubes with SWNTs-NIPA gel were placed inside a super-conducting magnet while the gel was polymerizing. The applied magnetic field aligned the nanotubes along the magnetic field before the nanotubes got locked into position by the NIPA gels. The entire sample looked strongly birefringent under cross- polarizers indicating high degree of alignment of nanotubes in the gels. Surprisingly, nanotubes chained up to form "nanotube needles" under the magnetic field were also observed. Fig. 12 shows such an image for a sample with initial SWNTs concentration of 0:78 mg/ml. The formation of nanotube needles depended on the initial nanotube concentrations in gel, applied magnetic field strength, gel viscosity, and the presence or absence of iron in the carbon nanotubes. Carbon nanotubes containing iron readily aligned in a 9 T magnetic field. The gel viscosity was controlled by varying the NIPA monomer and the cross-linker concentrations. Lower gel viscosity allowed the nanotubes to move in the gel during the polymerization process to form long needles. Shrinking this gel did not destroy the nanotube needles, rather increased their number density and also slightly increased the birefringence of the sample.

[0140]   **Other gels and suspending materials.** SWNTs were also dispersed in water, poly(methyl methacrylate) (PMMA) gel and poly(vinyl acetate) gel (PVA). Nanotube ropes with a length distribution of from 30 μm to 2 cm were obtained in water. In PMMA and PVA gel, SWNTs formed similar structures as those formed in NIPA gels.

[0141]   **Uses of Nematic Nanotube Gels.** Nematic nanotube gels can be used to create high quality composites for various applications. Examples are provided below.

[0142]   **Polymer composites containing nematic nanotubes.** Nanotubes are dispersed and aligned in various types of polymer gels. The alignment approach is very useful because aligned nanotubes and nanotube needles can be readily formed in polymeric gels according to the methods described herein. As aligned nanotubes increase the strength and thermal properties of composites, composites having aligned nanotube needles should also be capable of dissipating heat.   Following the various orienting procedures described in these examples, polymer composites containing nematic nanotubes are prepared using an orienting field, such as stretching fibers and films of a rubbery polyester resin that contain SWNTs. In another example, polymeric composites of styrenic thermoplastics that contain nematic SWNT nanotubes are obtained by shearing styrenic thermoplastic fluids that

containing nanotubes at an elevated temperature, which is followed by cooling upon

cessation of the shearing. In another example, the nanotubes are oriented using a 1 T

magnetic field in a polymeric liquid, such as rubbery PMMA at an elevated temperature,

followed by cooling.

[0143] **Curable resins having nematic nanotube gels.** This example provides one

solution to incorporating aligned nanotubes in a curable resins, such as epoxies, at high

concentration. In this example, carbon nanotubes are dispersed in an epoxy and curing agent

gel precursor as described above. Curing is carried out in the presence of an orienting field,

such as a shear field arising from flow of the gel precursor dispersion in a microchannel

device. In another example, the orienting field is a magnetic field and the general procedures

described in Method 3, above, are used to orient the carbon nanotubes in the epoxy before the

solid matrix completely hardens. Such resulting cured resins containing nematic nanotubes

are useful in a variety of aerospace and semiconductor applications.